

Chapter → Thermodynamics and Thermochemistry

System → Part of Total universe
for which energy changes
are discussed.

represent
Matter (s, l, g)
Under study

Amount
fixed
(mass, moles)

Surrounding → Part of universe around
System is called surrounding.

Boundary (B) → Region which separates
System & Surrounding

B → can be real or Imaginary
→ flexible or Rigid
→ conducting or Insulator (Heat exchange possible)
(electrical) (electrical)
→ Thermally conducting or (Diathermic)
Thermally insulator
(Adiabatic Boundary)

no heat exchange b/w
System & surrounding

Depending upon Boundary type of system

open → Matter exchange ✓
Heat exchange ✓

closed → Matter exchange ✗
Heat " ✓

Isolated → Matter exchange ✗
Heat exchange ✗

No connection
with surrounding

Boundary is
adiabatic

Property of system

→ applicable for bulk of system / Macroscopic Nature
& not for a single particle (Microscopic nature)

→ Value of property is defined / obtained at Thermodynamic Eqⁿ state (condⁿ)

At Equilibrium,
state change is
opposed without
any external effect
Spiral

→ Total Bulk is defined
by single value of any
property.

Properties of system or properties of matter in system.

1) Intensive

- Properties which are independent of amount / mass of substance in system.

→ If we cut (System) or matter into 2 equal halves, value of property does not change.

egⁿ elasticity, Refractive index, density, ^{gas} Pressure, Temperature, molarity, Normality, electrode Potential, conductivity, Resistivity, molar heat capacity, specific heat capacity, molar Entropy, Molar Internal Energy (U or E), molar Mass (M), Gibbs free Energy (G), molar Enthalpy (H) etc.

2) Extensive (or Extrinsic)

→ Those properties whose value depend on amount of substance in system.

→ Cutting the system in two equal halves, value of property becomes half for each half of substance system.

egⁿ → mass, volume, Heat capacity (C), moles, C_p , S , H , etc.
Spiral

$E_{\text{ext}} = \text{Intensive}$
 E_{ext}

$U \rightarrow E_{\text{ext}}$ = molar Internal Energy (U_{m} or U_{m})
 mole $\rightarrow E_{\text{ext}}$ $\rightarrow E_{\text{int}}$

$m \rightarrow E_{\text{ext}}$ = density (Int.)
 $V \rightarrow E_{\text{ext}}$

$E_{\text{ext}} \times E_{\text{ext}} \neq \text{Int.}$

density = $\frac{\text{mass}}{\text{volume}}$

$E_{\text{ext}} - E_{\text{ext}} \neq \text{Int.}$

specific = $\frac{\text{Volume}}{\text{mass}}$ = $\frac{1}{\text{dens.}}$
 \downarrow
 $E_{\text{int.}}$

Thermodynamic state of system

→ at thermodynamic Eqⁿ, A state (condition) of Substance (Matter) in system specified by certain measurable macroscopic properties. (Int. or Ext.)

→ properties can be T, P, density, volume etc

Value of properties for a particular state remains fixed until thermodynamic Eqⁿ of system is maintained.

- ⑧ When state of system changes from one eqⁿ point to another eqⁿ point; value of properties at those states also changes & these properties at those states which are dependent only on the present state (irrespective of path taken to reach the state) are called state variables or functions or properties.

- ⑧ change in state function or variable
↓
depend only on initial and final state.

$$\Delta T = T_2 - T_1$$

↓
change in state function

⑧ Reversible expansion/
compression work → state
function

T → state function or variable

- ⑧ T, P, V etc → state variable / property

If (T) is obtained from values of P & V ^{independent variable} for any state then Temp. becomes variable state function for that state.

- ⑧ Path function → Function which depends on path taken to reach from one state of system to another state of system. egⁿ → Work, Heat, Heat capacity

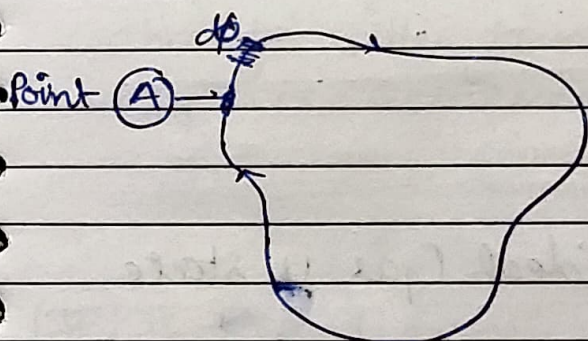
(#) Conditions for function to become state function

① Cyclic Integration is zero

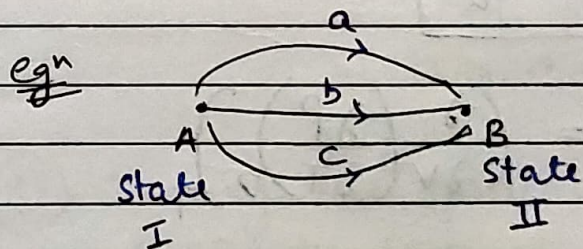
Initial State = final state

let ϕ is a function

If $\oint_A d\phi$ or $\oint d\phi = 0$, then ϕ is a state function



② B/w 2 states, change in state function is same for all the path taken



let ϕ is a function

for ϕ to be state function

$$(\Delta\phi)_a = (\Delta\phi)_b = (\Delta\phi)_c$$

③ Euler's reciprocity theorem must be satisfied

let ϕ is function of x & $y \Rightarrow \phi = f(x, y)$
~~for ϕ to be state funⁿ~~

$$\left[\frac{\partial}{\partial x} \left(\frac{\partial \phi}{\partial y} \right)_x \right]_y = \left[\frac{\partial}{\partial y} \left(\frac{\partial \phi}{\partial x} \right)_y \right]_x$$

Or

$$\left[\frac{\partial^2 \phi}{\partial x \partial y} \right]_{x, y}$$

① \rightarrow Prove Pressure of 1 mole ideal Gas is state function.

Solⁿ

$$PV = RT$$

$$P = f(V, T)$$

$$\boxed{P = \frac{RT}{V}}$$

$$\text{To prove: } \left[\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial V} \right)_T \right]_V = \left(\frac{\partial}{\partial V} \left(\frac{\partial P}{\partial T} \right)_V \right)_T$$

$$-\frac{R}{V^2}$$

$$-\frac{R}{V^2}$$

Hence Proved.

No change in
Date ... Pressure or
Process per unit time

⊕ Thermodynamic eq^n → Mechanical eq^n
(No pressure gradient)

Chemical eq^n Thermal eq^n
(No temp. gradient)

In Reversible Rx^n :-

No concentration gradient for
any species in Rx^n

↳ conc. of every species
becomes const. (does not
change with time) when
 eq^n is achieved

at this condⁿ only
we can find
value of any
macroscopic
property in
any state of
system.

⊕ Thermodynamic process :- Any method/process
by which system can
change its state from one state
of thermodynamic eq^n to another
thermodynamic eq^n .

⊕ During the process, value of any macroscopic
property cannot be defined.

⊕ If process occurs keeping any state property
const., then iso prefix is used.

→ Process occurs at const. Temp ; Isothermal
Process
 $T = \text{const.}$
 $\Delta T = 0$

Date

→ Process occurs at const vol; Isochoric Process $\Delta V = 0$
 $dV = 0$

→ " " " " Press. Isobaric Process $dP = 0$
 $\Delta P = 0$

→ Adiabatic process → No heat exchange b/w system & surrounding during the process.

$$Q \text{ or } q = 0$$

→ Cyclic Process → Initial state = final state

$$\text{Change in state funct} = 0$$

$$\text{Work done or heat exchange} \neq 0$$

⊕ Classification of thermodynamic processes on the Basis of the way these processes are carried out :-

① Reversible Process

If a process is carried out in such a manner so that the system is always in thermodynamic eqⁿ at every stage of the process.

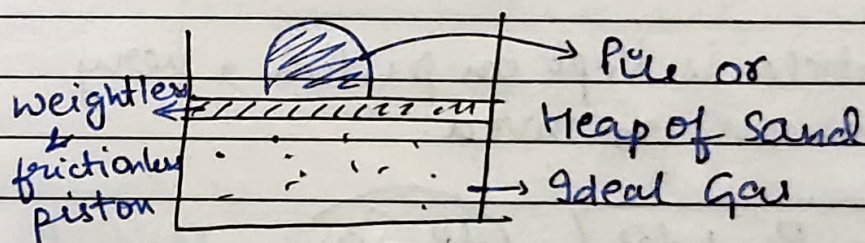
or

If the process is carried out such that the difference is driving force and opposing is infinitesimally small. So, that process takes place at infinitesimally slow rate.
 \hookrightarrow negligibly

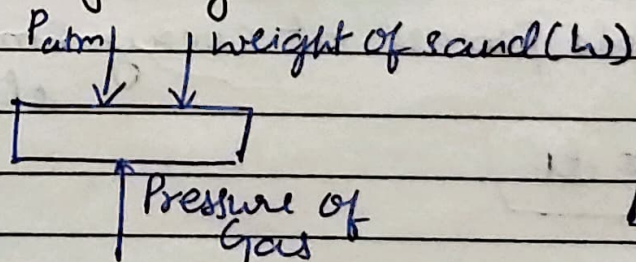
$$F_{\text{driving}} = F_{\text{opposing}} \pm df \quad \boxed{df \rightarrow 0}$$

① An ideal Reversible Process will take infinite time for completion \rightarrow reaching from initial state to required final state.

② Let's consider an example \div



Initially system at Rest (Eqn)



$$\boxed{P_{\text{atm}} + \frac{W}{A} = P_g}$$

\hookrightarrow Area

- If one sand particle is removed such that Eq^n is not disturbed b/w system & surrounding.

piston moves upwards giving infinitesimally small volume change due to small diff in opposing Pressure (P_{ext}) and (External)

Pressure of Gas
(driving force)

for negligible expansion of Gas

$$P_{ext} = (P_{int}) - dP \quad dP \rightarrow 0$$

P_g

very small step of expansion

- (**) If one sand particle is kept on piston, very small compression is observed.

$$P_{ext} = P_g + dP \quad (dP \rightarrow 0)$$

So, for Reversible process at every small step

$$P_{ext} = P_g \pm dP$$

(2) Irreversible process :-

If process is carried out in such a manner so that the system is in thermodynamic

equilibrium only at initial and final state of the process.

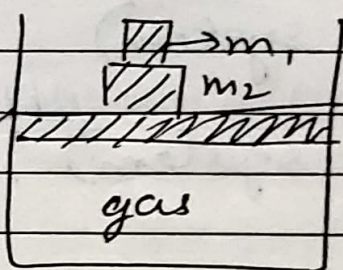
(**) There will be no equilibrium b/w system & surrounding during process.

(**) Steps are Big involving Big change in macroscopic properties.

(**) Irreversible can be completed in finite steps (1, 2, 3, ...)

(**) Diff. b/w opposing force & Driving force is finite.

egⁿ



• If m_1 is removed

P_{ext} (opposing Press) is $P_{\text{atm}} + \frac{m_2 g}{A}$

& gas expands under this Pressure $\left[P_{\text{atm}} + \frac{m_2 g}{A} \right]$

Initially $P_g \neq P_{\text{ext}}$

So, P_{ext} remain const.

$P_{\text{atm}} + \frac{m_1 g}{A} + \frac{m_2 g}{A}$ during any step of process.

• If m_2 is also removed, gas expands under

$$P_{\text{ext}} = P_{\text{atm}}$$

$$\text{till } P_g = P_{\text{ext}} = P_{\text{atm}}$$

★ Heat and Work :- Two ways by which system can interact or can exchange energy with its surroundings

Heat :- Energy exchange due to temp. diff. b/w syst. & surr.

Work :- Energy exchange takes place not due to temp. diff. but due to difference in opposing force & driving force.

Sign Convention

$q = +ve$ (Heat absorbed by system)

$q = -ve$ (Heat released by system)

Chemistry → we are external (surrounding)

System

(Expansion of gas)

W. done by system = $-ve$

W. done by surrounding = $+ve$

(Compression)

Physics → we are inside system or we are system.

W. done by system = $+ve$ (Expansion)

" " on system = $-ve$ (Compression)

Internal Energy (E or U)

Sum of all possible ~~value~~ forms of Energy associated with matter in any thermodynamic state of system at given Temp.

Extensive

$$U = K.E + P.E + \dots$$

State function

\approx Translational K.E + Rotational K.E + Vibrational K.E + Attractive Energy + Repulsive Energies + Bond Energy + ...

Energy due to External field effect is not considered

gravitational field, magnetic etc.

Absolute value of U cannot be determined we always find change of U by FLOT. (First law of Thermo.)

for ideal gas,

No interaction b/w gas molecules P.E.

$U = \boxed{K.E} \rightarrow$ only dependent of Temp.

U is function of T only for Ideal Gas.

$$\Delta U = \Delta k \cdot E$$

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 = \left(\frac{\partial U}{\partial P} \right)_T \text{ for ideal Gas}$$

for Real Gas,

U is function of (T, P, V)

$$\left(\frac{\partial U}{\partial V} \right)_{T,P} \neq 0$$

$$\left(\frac{\partial U}{\partial P} \right)_{T,V} \neq 0$$

Law of equipartition of Energy :-

* Energy equal to $\frac{1}{2} kT$ is associated with each degree of freedom per ideal Gas molecule.

(Dof) Degree of freedom \rightarrow No. of ways in which energy of molecule can be distributed.
or
f

Types :-

(i) f_T (Translational dof)

(ii) f_R (Rotational dof)

vibratⁿ in Bond occur at High Temp.

(iii) f_V (Vibrational dof)

$T \approx 500^\circ\text{C}$ or above

$$f_T + f_R + f_V$$

* Total Dof (f) for any molecule = $3N$
No. of atoms in molecule

at Room Temp, only $f_T + f_R$ exist

$$f_T = 3$$

a) Monoatomic Gas ÷

$$f_R = 0, f_V = 0, \boxed{f_T = 3} \Rightarrow \text{along } x, y, z$$

egⁿ → He, Ne, ~~Ar~~ etc

↳ always for every type of gas

$$\rightarrow \text{Total D.o.f} = 3N = 3 \times 1 = 3$$

b) Diatomic Gas ÷ $\boxed{f_T = 3}$ $\boxed{f_R = 2}$ $\boxed{f_V = 1}$

egⁿ → CO, O₂, Cl₂, Br₂ etc

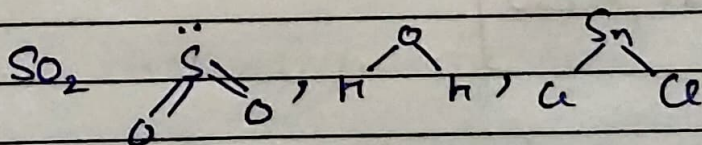
$$\rightarrow \text{Total D.o.f} = 3 \times 2 = 6$$

c) Triatomic Gas → Triatomic Linear (Like $\text{O}=\text{C}=\text{O}$, $\text{F}-\text{Xe}-\text{F}$) (Diatomic)
CO₂, XeF₂

$$f_T = 3, f_R = 2, f_V = 4$$

↓
Triatomic Non-Linear

$$f_T = 3, f_R = 3, f_V = 3$$



d) Polyatomic Gas $\Rightarrow f_T = 3, f_R = 3, f_V = 3N - 6$

$$\text{Total} = 3N$$

for 1 d.o.f, $\overline{K.E}$ or $E = \frac{1}{2} kT$ per molecule

$$= \frac{1}{2} RT \text{ per mole}$$

at Room Temp.

for f dof, $\overline{K.E} = \frac{f}{2} kT$ per molecule of Gas
 $\rightarrow f_T + f_R$

$$= \frac{f}{2} kT \text{ per molecule}$$

$f_V \rightarrow$ neglected

$$\Delta \overline{K.E} = \Delta U \quad (\text{for Ideal Gas})$$

$$\boxed{\frac{f}{2} R(\Delta T) = \Delta U} \rightarrow \text{for 1 mole}$$

for n mole of Ideal Gas

$$\boxed{\frac{f}{2} n R \Delta T = \Delta U}$$

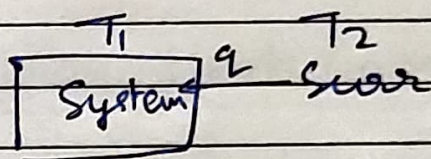
$$\boxed{f = f_T + f_R} \begin{aligned} &\approx 3 \text{ (mono)} \\ &\approx 5 \text{ (Di or Tri linear)} \\ &\approx 6 \text{ (Tri Non-linear)} \end{aligned}$$

(#) Heat (q or Q) \div ~~etc~~

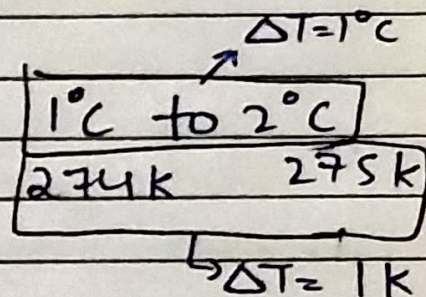
Energy flows or energy exchange b/w System and surrounding due to Temp. difference

System \Rightarrow Temp. of System Ted from T_1 to T_2

Heat (q) from surrounding to system is transferred due to temp. difference ($\Delta T = T_2 - T_1$)



$T_2 > T_1$



$$C = \frac{q}{\Delta T} \leftarrow 1^\circ\text{C}$$

Heat capacity of Substance in System

Specific Heat capacity (s) \Rightarrow $s = \frac{C}{\text{mass}}$

Molar Heat Capacity (C_n)

$$\frac{C}{m/m} = \frac{C}{\text{mole (n)}} = C_n = \frac{q}{n \times \Delta T}$$

$$\boxed{\frac{M \cdot C}{m} = C_n} = \boxed{M \cdot s} \rightarrow \text{intensive}$$

①

$$\boxed{\begin{array}{l} \text{Al} \leftarrow 30\text{J} \\ 9\text{g} \end{array}} \quad 25^\circ\text{C to } 31^\circ\text{C}$$

$$C = \frac{30}{6} = 5 \text{ J/K or } 5 \text{ J/}^\circ\text{C}$$

$$s = \frac{5 \text{ J K}^{-1} \text{ gm}^{-1}}{9}$$

$$C_n = \frac{5 \times 9^3}{9} = 15 \text{ J K}^{-1} \text{ mol}^{-1}$$

#

$$q \leftarrow \Delta T (^\circ\text{C or K})$$

$$\left(\begin{array}{l} \text{Heat} \\ \text{Capacity} \end{array} \right) C = \frac{q}{\Delta T} \leftarrow 1(^\circ\text{C or K})$$

$$\Downarrow$$

$$\text{unit} = \text{J/K}$$

$$\text{or}$$

$$\text{J/}^\circ\text{C}$$

amount or mass
dependent
(Extensive)

Specific Heat capacity of substance (s)

Heat required by substance to change its temp. by 1°C or K for 1 gram substance

$$s = \frac{q}{m\Delta T} = \frac{C}{m} \rightarrow \text{Heat capacity}$$

↓
defined for given mass

↘ mass of substance

Unit $\rightarrow \text{J}(\text{}^\circ\text{C})^{-1}\text{gm}^{-1}$ or $\text{JK}^{-1}\text{gm}^{-1}$

Molar Heat Capacity (C_n)

Heat required to change temp. by 1°C or K for 1 mole substance.

$$C_n = \frac{q}{n\Delta T} = \frac{C}{n} = \frac{C}{m} \times M = \frac{C}{m} M$$

↘ moles of substance

$\text{JK}^{-1}\text{mol}^{-1}$

$n = \frac{\text{mass}(m)}{\text{Molar mass}(M)}$

Total Heat (q) exchange

$$= C\Delta T$$

$$= ms\Delta T$$

$$= nC_n\Delta T$$

Q \rightarrow find Total Heat absorbed by 100 g water when it is heated from 25°C to 45°C . $s(\text{water}) = 4.2 \text{ J}(\text{}^\circ\text{C})^{-1}\text{gm}^{-1}$

Soln

$$q = m \times s \times \Delta T$$

$$q = (100 \times 4.2 \times 20) J$$

$$= \frac{100 \times 4.2 \times 20 \text{ cal}}{4.18}$$

$$= \frac{100 \times 4.2 \times 20}{1000} \text{ KJ}$$

⑧ Molar Heat capacity (C_m) at

Const. Volume process $\rightarrow C_{m,v}$ or C_v .

⑧ Molar heat capacity (C_m) at

Const. Pressure process $\rightarrow C_{m,p}$ or C_p

⑧ Molar Heat Capacity $C_m \rightarrow \infty$ (for isothermal)

$$\Rightarrow \Delta T = 0$$

$\rightarrow 0$ (for adiabatic) $\Rightarrow q = 0$

for Solids/liq $\rightarrow C_p \approx C_v$

for gases $\Rightarrow C_v = \frac{q_v}{n\Delta T} \rightarrow$ Heat exchange at const. v

$C_p = \frac{q_p}{n\Delta T} \rightarrow$ Heat exchange at const P

⑧ Meyer's Relation

Relation b/w C_p & C_v

$$C_p - C_v = R$$

$$C_p = R + C_v$$

$\frac{C_p}{C_v} = \gamma$ (Poisson's Ratio)

$$\gamma > 1$$

$$C_p > C_v$$

$C_v = \frac{f}{2} R$

$$C_p = \left(\frac{f+2}{2} \right) R$$

$T =$ Moderate or Room Temp.

Atomicity of Gas

C_v

C_p

γ

Mono

$$\frac{3R}{2}$$

$$\frac{5R}{2}$$

$$\frac{5}{3} = 1.67$$

Dia or Tri(L)

$$\frac{5R}{2}$$

$$\frac{7R}{2}$$

$$\frac{7}{5} = 1.40$$

Tri (NL)

$$\frac{6R}{2} = 3R$$

$$\frac{8R}{2} = 4R$$

$$\frac{4}{3} = 1.33$$

Polyatomic

$$3R$$

$$4R$$

$$\frac{4}{3} = 1.33$$

$dq_v = dU$

$q_v = \Delta U = n C_v \Delta T \Rightarrow \frac{f}{2} n R \Delta T = n C_v \Delta T$

$$C_v = \frac{f}{2} R$$

$$C_v = \left(\frac{du}{dT} \right)_v = \left(\frac{dq}{dT} \right)_v$$

⊕ $q_p = (\Delta H) \rightarrow$ Enthalpy change

$$dq_p = dH$$

$$\left(\frac{dH}{dT} \right)_p = C_p = \left(\frac{dq}{dT} \right)_p$$

⊕ Heat capacity (C) \rightarrow is process dependent

\downarrow

J/°C
or
J/K

- \rightarrow path function
- \rightarrow Extensive property
- \rightarrow Temp. dependent

If Temp. dependency is not given, take Heat capacity of substance as temp. independent.

⊕ First law of Thermodynamics (FLOT)

"Energy is always conserved for universe."

or

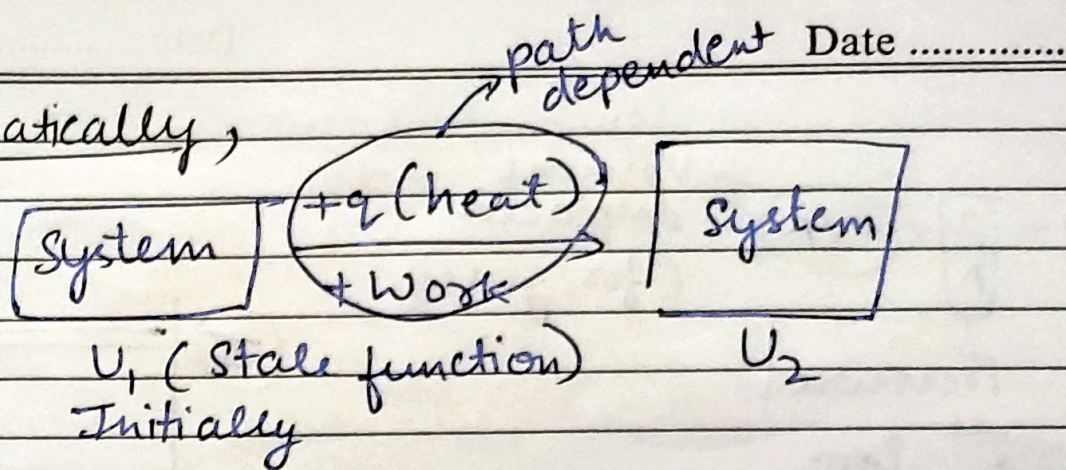
"Total energy for an isolated system remains constant."

or

"Energy can neither ~~not~~ be created nor be destroyed, it converts from one form to another form."

Spiral

Mathematically,



$$U_1 + q + W = U_2$$

$$U_2 - U_1 = q + W$$

$$\Delta U = q + W$$

$$\boxed{dU = \delta q + \delta W} \Rightarrow \text{Sum of two inexact differential can be exact differential}$$

or

$$\boxed{dU = dq + dW}$$

⊕ At const. Volume Isochoric process

$$W=0 \quad \boxed{\Delta U = q_v}$$

Q → What is change in Internal energy due when 40 KJ work is done on system & 20 KJ heat is released by system?

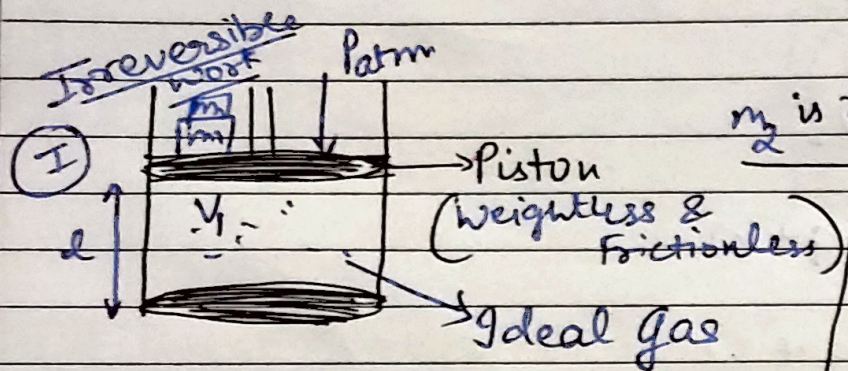
Solⁿ

$$\Delta U = \underbrace{q}_{-20} + \underbrace{W}_{+40} \rightarrow -20 + 40 = 20 \text{ KJ}$$

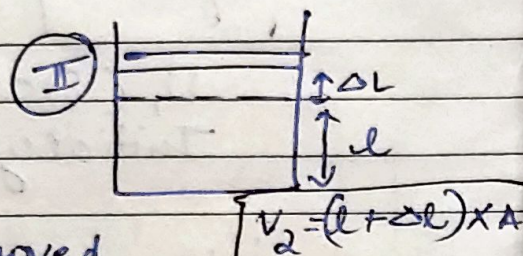
Work

$$W = \left[\frac{F}{A} \right] \times (d \times A) \rightarrow \text{Volume displaced (for gases)}$$

Pressure



$$V_1 = l \times A$$

 m_2 is removed

$$P_g > (P_{\text{ext}})_1$$

gas expansion will occur till

2 Vol. of gas becomes V_2 . $P_g = (P_{\text{ext}})_2$

$$= P_{\text{atm}} + \frac{m_1 g}{A}$$

Initially system is in Thermodynamic eqⁿ.

$$P_g = (P_{\text{ext}})_1 = P_{\text{atm}} + \frac{(m_1 + m_2)g}{A}$$

$$W_{\text{single step}} = -P_{\text{ext}} \cdot \Delta V$$

Ext. Press. during that step

vol. change of Gas in single step.

$$W_{I \text{ to } II} = -(P_{\text{ext}})_2 \cdot \Delta V$$

$$= -(P_{\text{ext}})_2 \cdot (V_2 - V_1)$$

(#) Note - Irreversible single
step work

$$= -P_{\text{ext}} \cdot \Delta V$$

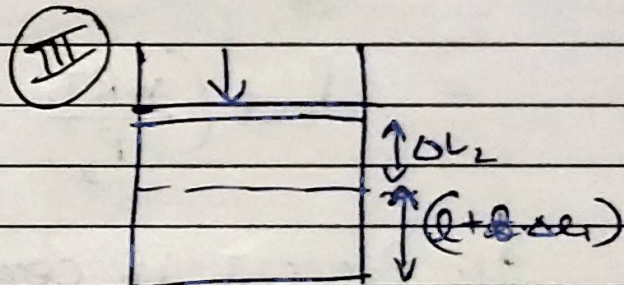
$$= -P_{\text{ext}} (V_2 - V_1)$$

$$= -P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

If process is complete,

$$P_{\text{ext}} = P_g$$

If m_1 is removed \rightarrow
gas expansion
occurs (w. done
by gas) to
achieve $(P_{\text{ext}})_3 = P_{\text{atm}}$



$$W_3 = (l + \Delta L_1 + \Delta L_2) \cdot A$$

$$W_{\text{II to III}} = (P_{\text{ext}})_3 (V_3 - V_2)$$

$$= -P_{\text{atm}} (V_3 - V_2)$$

If Both m_1 & m_2 are simultaneously removed, then Vol. of gas changes from $V_1 \rightarrow V_2$ under const. ext. Pressure of (P_{atm})

$$W_{\text{I tot}} = -P_{atm}(V_2 - V_1)$$

~~$$W_{\text{single step}} = -P_{ext} \Delta V$$~~

Note :-

Irreversible single step work

$$= -P_{ext} \cdot \Delta V$$

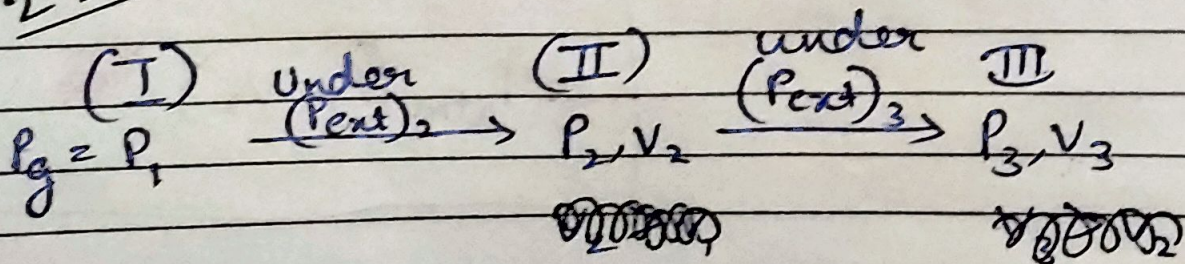
$$= -P_{ext}(V_2 - V_1)$$

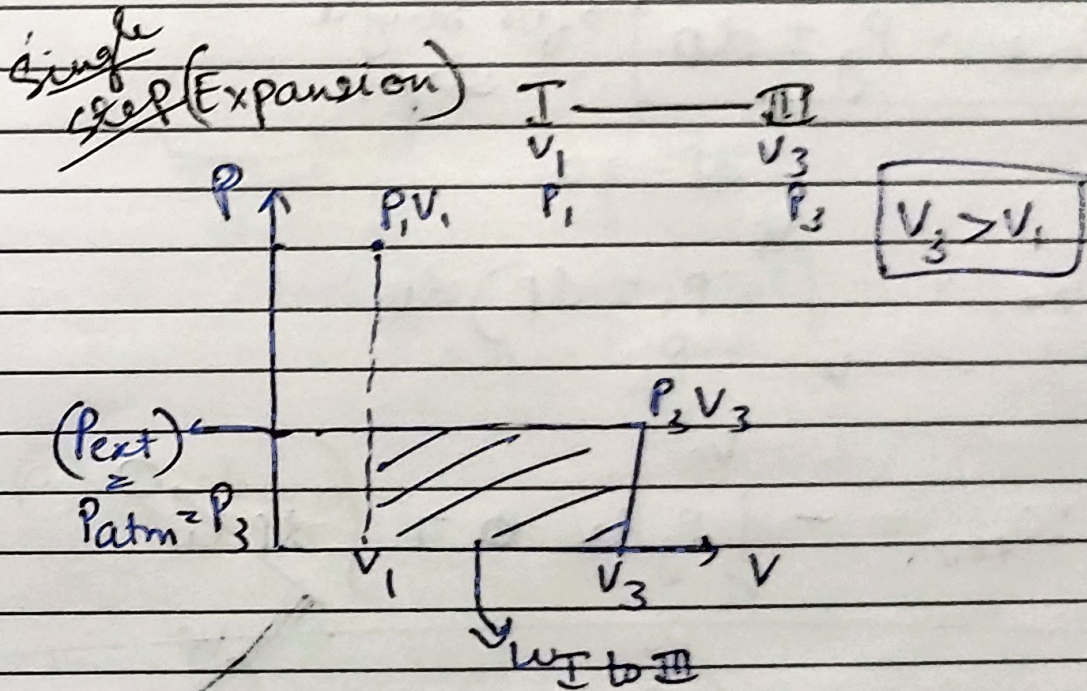
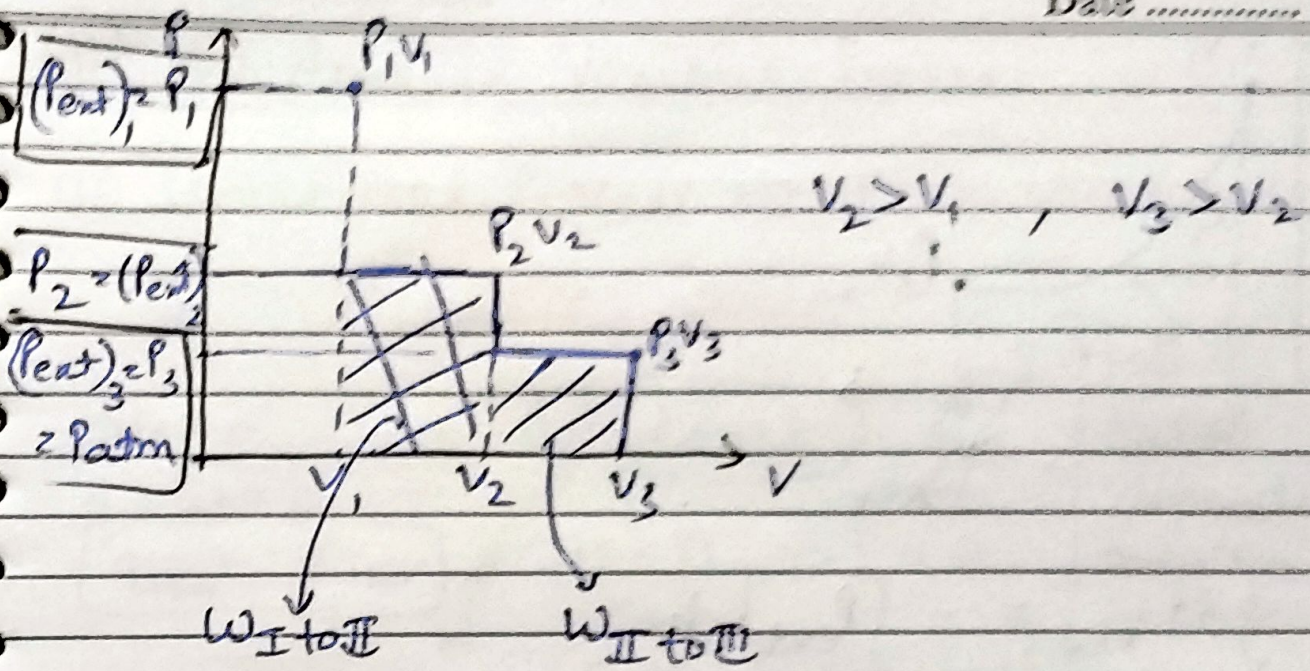
$$= -P_{ext} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

If Process is complete

$$P_{ext} = P_2$$

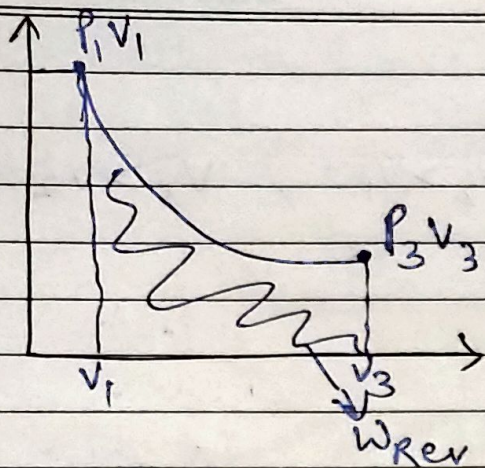
2 step work (Expansion)





So, During Expansion (Irreversible)

$W_{\text{infinite steps}}$...	$W_{3\text{-step}}$	$>$	$W_{2\text{-step}}$	$>$	$W_{\text{single step}}$
or W_{rev} Spiral expansion		$W_{\text{irrev expansion}}$				



$$\int dw_{rev} = - \int P_{ext} \cdot dv$$

$$P_{ext} = P_g \pm dp \quad \rightarrow \text{for single step}$$

$$dp \rightarrow 0$$

$$W_{rev} = - \int_{V_i}^{V_f} (P_g \pm dp) dv$$

$$W_{rev} = - \int_{V_i}^{V_f} P_g dv \quad \text{or} \quad \int dp dv \rightarrow 0$$

$$W_{rev} = - \int_{V_i}^{V_f} P_g dv = - \int_{V_i}^{V_f} \frac{nRT}{V} dv$$

works for
both Exp or Compression

Note: Compression of Gas, V dec. $\boxed{W = +ve}$

$$|w_{\text{single step}}| > |w_{\text{2-step}}| > \dots > |w_{\text{infinite step}}| \text{ or } |w_{rev}|$$

W-done in Various Process① Isothermal Process $\Rightarrow T = \text{const.}$ $\Delta T = 0$

$$\Delta U = nC_v \Delta T = 0$$

$$\Delta U = 0$$

$$(U = \text{const.})$$

$$q + w = 0$$

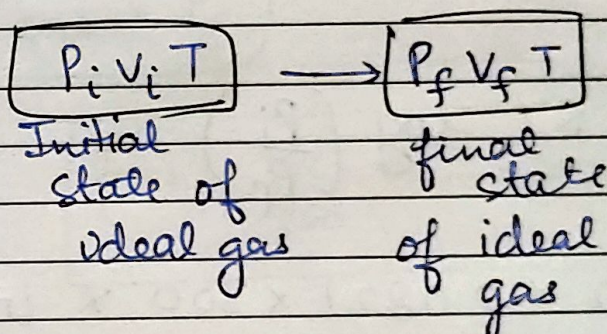
$$q_{\text{iso}} = -w_{\text{iso}}$$

$$\Delta H = nC_p \Delta T = 0$$

$$(\Delta H = 0) \quad H = \text{const.}$$

H & U

Both depends only on Temp. for Ideal Gas.



$$(a) (w_{\text{rev}})_{\text{iso}} = - \int_{V_i}^{V_f} nRT \frac{dV}{V}$$

$$= -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \left(\frac{V_f}{V_i} \right) = -nRT \ln \left(\frac{P_i}{P_f} \right)$$

or

$$= -2.303 nRT \log \left(\frac{V_f}{V_i} \right)$$

Boyle's law

$$P_i V_i = P_f V_f$$

$$\frac{V_f}{V_i} = \frac{P_i}{P_f}$$

Spiral

$$= -2.303 nRT \log \left(\frac{P_i}{P_f} \right)$$

$$(q_{iso})_{rev} = (-W_{iso})_{rev}$$

Q → find q , ΔU , W when 2 mole of ideal undergoes Reversible isothermal process to change its state from (1 atm, 300K) to (3 atm, 300K)?

$$R = 0.0821 \text{ or } \frac{1}{12} \text{ L-atm mol}^{-1} \text{ K}^{-1}$$

Solⁿ

$$\Delta U = 0$$

$$q_{rev} = -W_{rev}$$

$$W_{rev} = -2.303 n RT \log \left(\frac{P_i}{P_f} \right)$$

$$= -2.303 \times 2 \times 0.0821 \times 300 \times \log \left(\frac{1}{3} \right)$$

$$= +2.303 \times 2 \times 0.0821 \times 300 \times 0.47 \text{ L-atm}$$

$$1 \text{ L-atm} = 101.325 \text{ Joule}$$

$$\log 2 = 0.3$$

$$\log 3 = 0.47$$

$$\log 5 = 0.7$$

$$\log 7 = 0.84$$

$$\log 11 = 1.043$$

$(W_{rev})_{\text{compression}}$

$$= 2.303 \times 2 \times 0.0821 \times 300 \times 0.47$$

$$\times 101.325 \text{ Joules}$$

(b) single step

$$W_{irr} = -P_{ext} (V_f - V_i)$$

$$= -P_{ext} \left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right)$$

$$(W_{irr})_{iso} = -P_{ext} nRT \left[\frac{1}{P_f} - \frac{1}{P_i} \right]$$

** When Exp. or compression completes

$$P_{ext} = P_f$$

$$(W_{irr})_{iso} = -nRT \left[1 - \frac{P_f}{P_i} \right]$$

Q → find ΔU when 20 kJ heat is given to ideal Gas & gas expands under Ext Press. of 2 atm from 3 dm³ to 5 dm³?

Solⁿ

$$\Delta U = q + w$$

$$\Delta U = 20 - P_{ext} \Delta V$$

$$= 20 \text{ (kJ)} - 2 \underbrace{(5-3)}_{\text{dm}^3} \text{ atm}$$

$$\Delta U = 20 \times 10^3 \text{ J} - (2 \times 2 \times 101.325) \text{ J}$$

② Adiabatic Process

$$P_1 V_1 T_1 \rightarrow P_2 V_2 T_2$$

\Rightarrow System having ideal Gas is isolated

$\Rightarrow q = 0 \rightarrow$ Heat exchange $= 0$

$$\Rightarrow \Delta U = q + w$$

$$\Delta U = W_{ad} = n C_v (T_2 - T_1) \rightarrow \text{Rev or Irr.}$$

~~$$\Delta U = n C_v (T_2 - T_1)$$~~

$$C_p - C_v = R$$

$$\frac{C_p}{C_v} - \frac{C_v}{C_v} = \frac{R}{C_v}$$

$$\gamma - 1 = \frac{R}{C_v}$$

$$C_v = \frac{R}{(\gamma - 1)}$$

$$W_{ad} = \frac{nR}{(\gamma - 1)} \left[\frac{P_2 V_2}{nR} - \frac{P_1 V_1}{nR} \right]$$

$$W_{ad} = \frac{P_2 V_2 - P_1 V_1}{(\gamma - 1)} = \frac{\Delta(PV)}{(\gamma - 1)}$$

Adiabatic Exp. of Gas

$$\rightarrow W_{ad} = -ve$$

$$nC_v(T_2 - T_1) = -ve$$

$$(T_2 < T_1) \quad T \downarrow \text{es, Cooling}$$

Adiabatic Compression of Gas

$$W_{ad} = +ve$$

$$\Delta T = +ve$$

$$(T_2 > T_1) \quad T \uparrow \text{es, Heating}$$

If During Calculation of Work, any parameter is not given then, we must know whether Process is Rev. or Irr. .

(a) Process is Rev. Ad.

$$dU = (dW_{ad})_{rev}$$

$$nC_v dT = - \int nRT \frac{dV}{V}$$

$$nC_v \int \frac{dT}{T} = -nR \int \frac{dV}{V}$$

$$nC_V \ln\left(\frac{T_2}{T_1}\right) = -nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_V} \ln\left(\frac{V_2}{V_1}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = (\gamma - 1) \ln\left(\frac{V_2}{V_1}\right)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{(\gamma - 1)}$$

$$TV^{\gamma-1} = \text{const.}$$

Similarly,

$$PV^{\gamma} = \text{const.}$$

$$T^{\gamma} P^{1-\gamma} = \text{const.}$$

(b) Irr. Ad

$$\Delta U = W_{ad}$$

$$nC_V(T_2 - T_1) = -P_{ext}(V_2 - V_1)$$

$$nC_V(T_2 - T_1) = -P_{ext} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

Q → 3 mole of non-linear triatomic Gas undergoes adiabatic process such that state of Gas changes from

$$\boxed{16 \text{ atm}, 300 \text{ K}} \longrightarrow \boxed{1 \text{ atm}, T(\text{K})}$$

2 work
find T if (i) Process is Reversible
(ii) Process is Irreversible

Solⁿ (i) Reversible

$$W_{\text{ad}} = nC_V(T_2 - T_1) = 3 \times 3R [T - 300]$$

T value for Reversible Process

$$T^{\gamma} P^{1-\gamma} = \text{const.}$$

$$T_1^{\gamma} P_1^{1-\gamma} = T_2^{\gamma} P_2^{1-\gamma}$$

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{1-\gamma} \Rightarrow T_2 = T_1 \left[\frac{P_1}{P_2}\right]^{\frac{1-\gamma}{\gamma}}$$

$$T = T_2 = 300 \left[\frac{16}{1}\right]^{\frac{1-\frac{4}{3}}{\frac{4}{3}}} = 300^{\frac{1}{4}}$$

$$= 300 (2^4)^{\frac{1}{4}}$$

$$= \frac{300 \times 2}{2} = \boxed{150 \text{ K}}$$

$$(W_{ad})_{Rev} = 3 \times 3R [150 - 300] = 9R \times (-150) \text{ Joules}$$

(ii) Process is Irr

$$(W_{ad})_{irr} = 3 \times 3R (T - 300)$$

T is calculated from irreversible path using eqⁿ (1) or (2)

$$-1 \times R \left[\frac{T}{1} - \frac{300}{16} \right] = 3R [T - 300]$$

$$T \approx 236 \text{ K}$$

$$(W_{ad})_{irr} = 3 \times 3R (T - 300)$$

$$= 3 \times 3R (230 - 300) \\ = 9R (-70)$$

(cooling)

Conclusion

Initial state

P_1, V_1, T_1

Adiabatic

Rev. Exp.

$P_2, V_2, (T_{rev})_{final}$

(cooling)

Ad

Irr Exp.

$$|(\Delta T)_{rev}| > |(\Delta T)_{irr}|$$

$P_2, V_2, (T_{irr})_{final}$
(ΔT_{rev})

$$T_1 > (T_{irr})_{final} > (T_{rev})_{final}$$

(ΔT)_{irr}

① Comparison b/w Iso & Adiabatic

$$\text{Expansion} \quad |W_{\text{iso}}| > |W_{\text{ad}}| \quad (\text{Rev. or Irr.})$$

② Isochoric Process

$$V = \text{const.}$$

$$\Delta V = 0$$

$$W = 0$$

from FLOT

$$q + w = \Delta U$$

$$q_v = \Delta U = nC_v \Delta T$$

④ Isobaric Process

$$P = \text{const.}$$

$$dw = -P_{\text{ext}} dv$$

$$w = -P \int dv$$

$$W = -P \Delta V$$

$$\boxed{W = -P \Delta V}$$

$$W = -nR \Delta T$$

→ gas undergoes expansion or compression

① for R_x^n

T, P, V

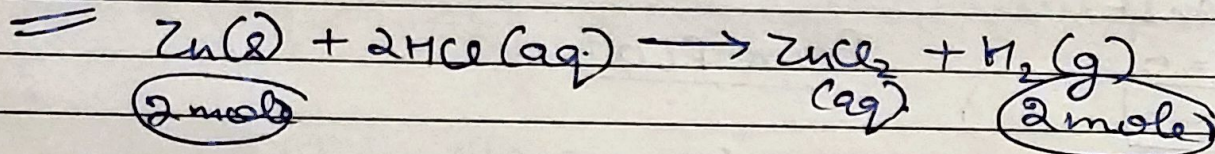
→ kept const. when we set any R_x^n .

Work done in case of R_x^n is due to change in

moles of Gaseous Species

$$W = -P\Delta V = -(\Delta n_g)RT$$

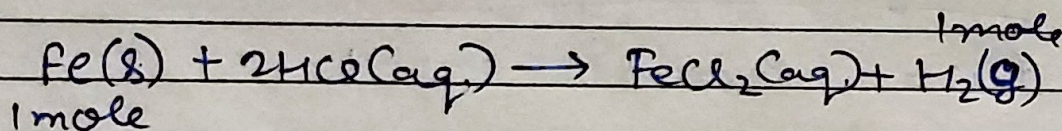
Q → find work done in (Joule) when 2 mole Zn is dissolved in HCl in 25°C? $[R = 8.314 \text{ J/K/mole}]$

Solⁿ

W. done by system = W. done by H₂ gas = ~~0~~ $-\Delta n_g RT$

$$= (2-0) \times R \times T$$

↳ initial moles
 ↳ final of H₂
 moles of H₂

Q-101
(Pg-48)

$$\begin{array}{ccc} 50 \text{ mole} & & 50 \\ 55.85 & \xrightarrow{\quad} & 55.85 \end{array}$$

$$W = -\Delta n_g RT$$

$$= \frac{50}{55.85} \times 8.314 \times 298 \text{ Joule}$$

H (Enthalpy)

- State function
- Extensive property
- Defined as $H = U + PV$

$$dH = dU + d(PV)$$

$$dH = dU + PdV + VdP \quad \text{at const. } P$$

from 1st law

$$dq + dw = dU$$

$$dq_p - PdV = dU$$

$$dq_p = dU + PdV$$

at const. P

$$dH = dq_p \Rightarrow q_p = \Delta H$$

heat exchange b/w system & surrounding at const. P is enthalpy change

a) Nothing is const.

$$dH = dU + d(PV)$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

for ideal gas $\Delta H = \Delta U + (nRT_2 - nRT_1)$

$$\Delta H = \Delta U + nR(T_2 - T_1)$$

b) at const P, $\Delta H = \Delta U + P\Delta V$

Ideal Gas
undergoing any
Process
(Exp or Comp.)

$$\Delta H = \Delta U + nRT$$

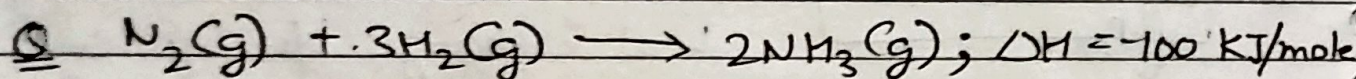
c) for Rxn involving Ideal Gases

$$P\Delta V = \Delta n_g RT$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H - \Delta U = \Delta n_g RT$$

$$q_p - q_v = \Delta n_g RT$$



a) find heat evolved at const. Volume at 300K?

$$q_v = \Delta U$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta U = \Delta H - \Delta n_g RT$$

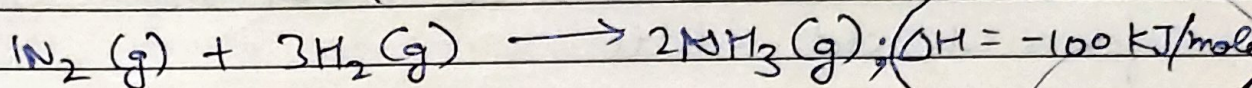
$$\Delta n_g = 2 - (3+1) = -2$$

Difference of stoichiometric
coeff. of product & reactant

$$\Delta U = \Delta H + 2RT$$

$$= [-100000 + 2 \times 8.314 \times 300] \text{ Joule}$$

b) find heat evolved at const. Volume when 4 moles of N_2 and 12g of H_2 reacts at 300K?



$$\begin{array}{r} 4 \text{ mole} \\ = 2 \\ \hline 2 \end{array}$$

$$\begin{array}{r} 12 \text{ g mole} \\ 2 \\ \hline -6 \\ \hline 0 \end{array}$$

$$\begin{array}{r} 0 \\ + 4 \\ \hline 4 \end{array}$$

A/c to
stoch. coeff.
of (L.R)

$$\Delta U = \Delta H - \Delta n_g RT$$

$$\Delta U = [-100 \times 10^3 - (-2)RT]$$

w.r.t 3 moles of L.R

$$\text{w.r.t 3 mole of L.R} \rightarrow \Delta U = [-100 \times 10^3 + 2RT]$$

$$\text{" 1 mole " " " } \rightarrow \Delta U = \frac{[-100 \times 10^3 + 2RT]}{3}$$

$$\text{" 6 mole " " " } \rightarrow \Delta U = \frac{(-100 \times 10^3 + 2RT)}{3} \times 6$$

Thermochemistry

We will deal with ΔH of various Rx^n / phase change

$$\Delta H_{Rx} = -ve \text{ (exo)}$$

$$\Delta H_{Rx} = +ve \text{ (endo)}$$

(I) Std. Enthalpy of formation (ΔH_f°)

Spiral

Temp. usually taken 25°C

$P = 1 \text{ bar}$
Conc = 1 mole

Standard state

Enthalpy change (usually -ve) when 1 mole substance (s, l, g) is formed from its constituent elements present in their most stable form at std. state.

$$\Delta H_f^\circ (\text{Elemental form}) = 0$$

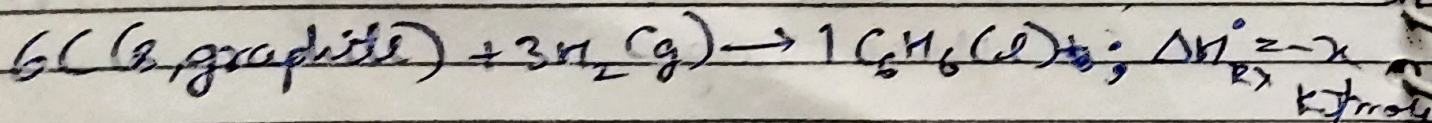
- $\Delta H_f^\circ (\text{C, s, graph.}) = 0$
 - $\Delta H_f^\circ (\text{C, s, diamond}) \neq 0$
 - $\Delta H_f^\circ (\text{H}_2, \text{g}) = 0$
 - $\Delta H_f^\circ (\text{H, g}) \neq 0$
 - $\Delta H_f^\circ (\text{S}_8, \text{rhombic}) = 0$
 - $\Delta H_f^\circ (\text{S}_8, \text{Monoclinic}) \neq 0$
 - $\Delta H_f^\circ (\text{H}^+, \text{aq.}) = 0$ (Assume)
 - $\Delta H_f^\circ (\text{OH}^-, \text{aq.}) \neq 0$
- rhombic is more stable than Monoclinic form at RT (25°C)

- $\Delta H_f^\circ (\text{Br}_2, \text{l}) = 0$
- $\Delta H_f^\circ (\text{Br}_2, \text{g}) \neq 0$
- $\Delta H_f^\circ (\text{O}_2, \text{g}) = 0$
- $\Delta H_f^\circ (\text{Cl}_2, \text{g}) \neq 0$
- $\Delta H_f^\circ (\text{O}_2, \text{g}) = 0$

Exception

$$\begin{aligned} \Delta H_f^\circ (\text{White P.}) &> 0 \\ \Delta H_f^\circ (\text{Red P.}) &\neq 0 \\ \Delta H_f^\circ (\text{Black P.}) &\neq 0 \end{aligned}$$

stability order = white P < Red P < Black P



$$= \Delta H_f^\circ (\text{C}_6\text{H}_6, \text{l})$$

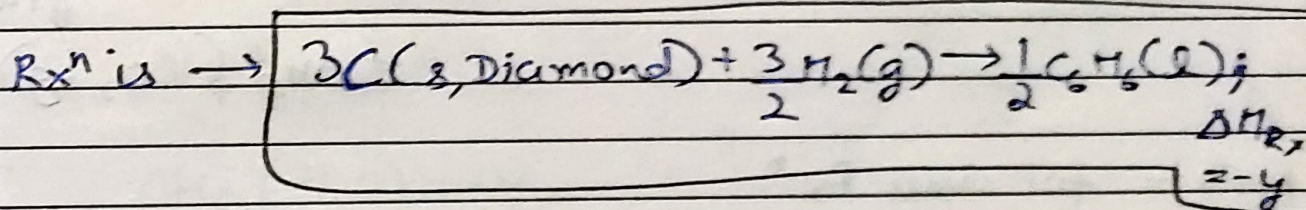
$$-x = \Delta H_{\text{rx}}^\circ = 1 \Delta H_f^\circ (\text{C}_6\text{H}_6) - [6 \cancel{\Delta H_f^\circ (\text{C, s, graph.})} + 3 \cancel{\Delta H_f^\circ (\text{H}_2)}]$$

Note ÷ for any Rxn

$$\Delta H_{Rxn} = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$$

Q find ΔH_f of (C_6H_6) ?

$$\Delta H_f(C, s, \text{Diamond}) = -x \text{ kJ/mole}$$



Solⁿ $\Delta H_{Rxn} = -y = \frac{1}{2} \Delta H_f(C_6H_6) - 3 \Delta H_f(C, s, \text{diamond}) - \frac{3}{2} \Delta H_f(H_2, g)$

$$-y = \frac{1}{2} \Delta H_f(C_6H_6) - 3(-x)$$

$$2(-3x - y) = \Delta H_f(C_6H_6)$$

② ΔH_c° (Std. Enthalpy of Combustion)

↳ Enthalpy change (usually -ve) when 1 mole substance (s, l, g) is completely burnt in oxygen at Std State.

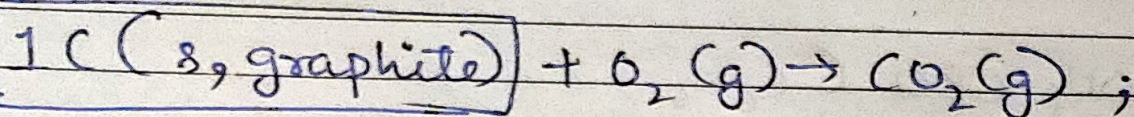
Date

$\Delta H_c = +ve$ only
for F_2, N_2, N_2O

$$\Delta H_c(O_2) = 0$$

$$\Delta H_c(CO_2) = 0$$

$$\Delta H_c(H_2O) = 0$$



$$\Delta H_R = -x = \Delta H_c^\circ(C, s, \text{graphite})$$

$$= \Delta H_f^\circ(CO_2, g)$$

Note - for any Rx^n

$$\Delta H_R = \sum \Delta H_c(\text{Reactants}) - \sum \Delta H_c(\text{Products})$$

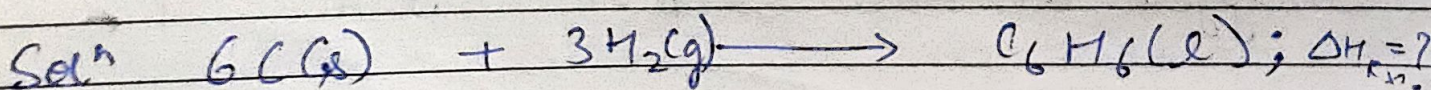
$$\Delta H_R = \Delta H_c(C, s, \text{grap.}) + \cancel{\Delta H_c(CO_2)} - \cancel{\Delta H_c(CO_2)}$$

$$\Rightarrow \Delta H_f(C_6H_6, l) = ?$$

$$\Delta H_c(C_6H_6, l) = -x$$

$$\Delta H_c(H_2, g) = -y$$

$$\Delta H_c(C, s, \text{graphite}) = -z$$



Date

$$6\Delta H_c(C, s) + 3\Delta H_c(H_2) - \Delta H_f(C_6H_6) = 1 \times \Delta H_f(C_6H_6) - [6\Delta H_f(C, s) + 3\Delta H_f(H_2)]$$

$$6(-z) + 3(-y) - (-x) = \Delta H_f(C_6H_6)$$

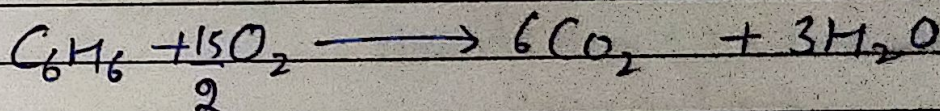
$$\boxed{-6z - 3y + x = \Delta H_f(C_6H_6)}$$

Q $\rightarrow \Delta H_c(C_6H_6, l) = ?$

$$\Delta H_f(CO_2) = -x$$

$$\Delta H_f(H_2O) = -y$$

$$\Delta H_f(C_6H_6) = -z$$



$$\Delta H_c(C_6H_6, l) = 6\Delta H_f(CO_2) + 3\Delta H_f(H_2O) - \Delta H_f(C_6H_6) - \cancel{\Delta H_f(O_2)}$$

$$= 6(-x) + 3(-y) - (-z)$$

$$= -6x - 3y + z$$

Q If x gm Benzene on combustion releases y kJ of heat. find enthalpy of combustion of Benzene?

Solⁿ $\left(\frac{x}{\text{molar mass of Benzene}} \right) \text{ moles} \longrightarrow -y \text{ KJ}$

1 mole $\longrightarrow \frac{-y}{x/M} \Rightarrow \frac{-yM}{x} \text{ KJ/mole}$ $\xrightarrow{\Delta H_c \text{ (Benzene)}}$

(#) Calorific value (cv) of substance $\xrightarrow{\text{Unit J/g or KJ/g or Cal/g}}$
 \hookrightarrow Heat evolved by combustion of 1gm substance.

(**) C.V of substance = $\frac{\Delta H_c \text{ (Substance)}}{\text{Molar mass of substance}}$

$\text{C}_2\text{H}_5\text{-OH}$
 Q $\rightarrow \Delta H_c \text{ (Ethanol)} = -x \text{ KJ/mole}$
 find C.V of ethanol?

Solⁿ 1 mole $\longrightarrow \Delta H_c = -x$
 $\hookrightarrow 46 \text{ g}$

1g $\longrightarrow \left(\frac{-x}{46} \right) = \text{C.V}$

(3) $\Delta H_{\text{neutralization}}$ $\xrightarrow{-ve}$

Std. enthalpy change

when 1 equivalent or 1gm-eq. Acid is neutralised

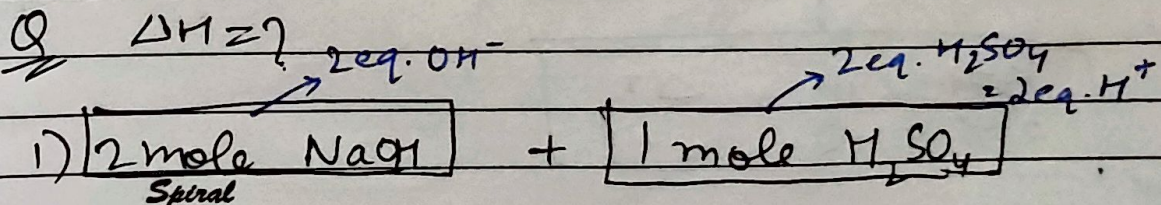
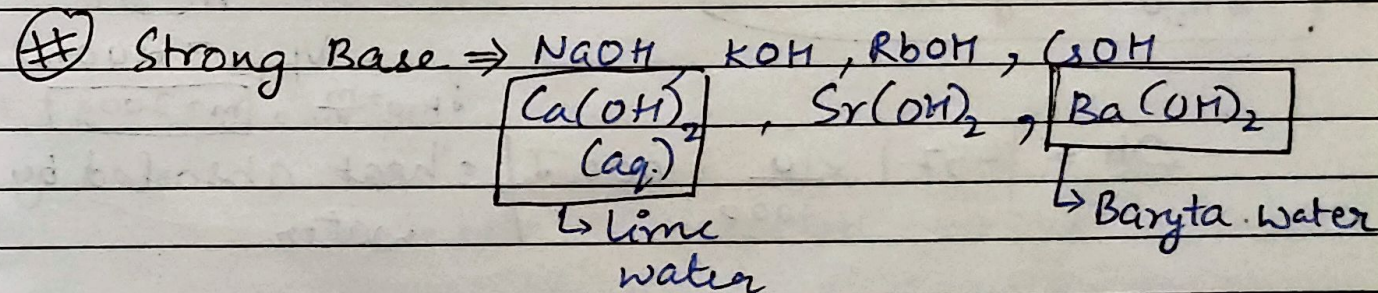
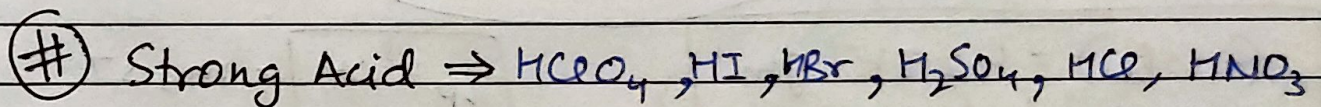
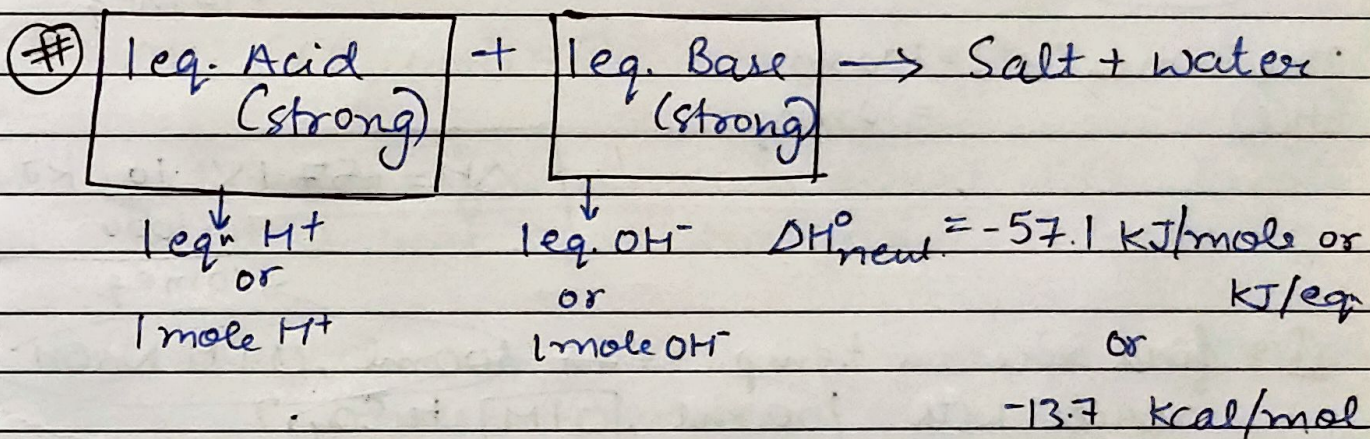
by 1 gm-eq of Base

$$\textcircled{\#} \frac{\text{gm-eq}}{\text{or eq}} = \text{mole} \times n.f$$

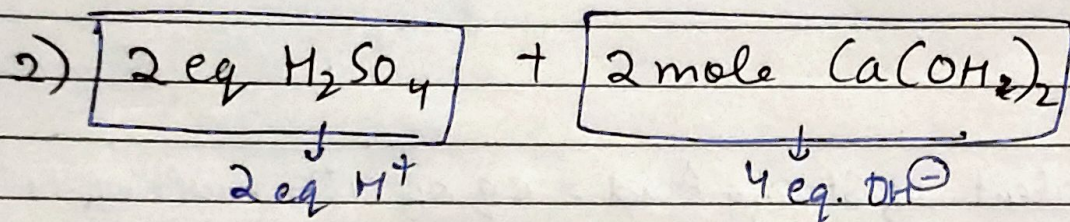
$$\textcircled{\#} \left\{ \begin{array}{l} \text{equivalent of Strong Acid} = \text{eq of } H^+ = \text{mole of } H^+ \\ \text{equivalent of Strong Base} = \text{eq of } OH^- = \text{mole of } OH^- \end{array} \right.$$

$$\textcircled{\#} \text{eq.} = N \times V_{\text{soln}} (L) \quad \boxed{N = M \times n.f}$$

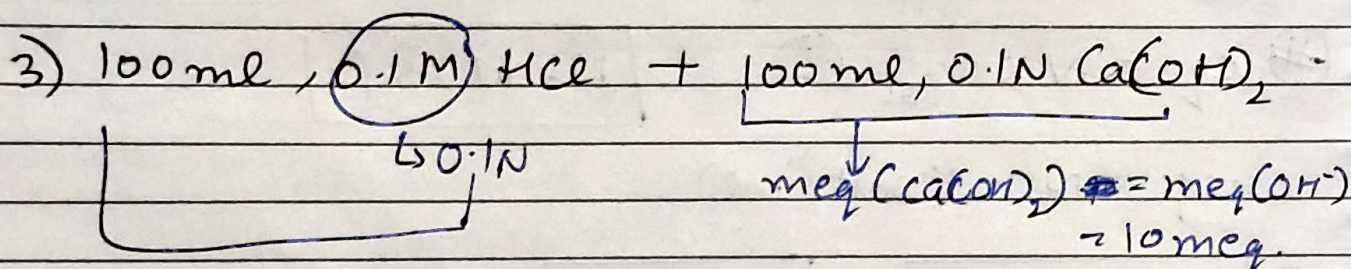
$$\text{meq.} = N \times V_{\text{soln}} (ml)$$



$$\text{Sol}^n \quad \Delta H = (-57.1 \times 2) \text{ KJ}$$



$$\Delta H = (-57.1 \times 2) \text{ KJ}$$



$$\text{meq} = \text{meq}(\text{H}^+) = 100 \times 0.1 = 10 \text{ meq}$$

(HCl)

$$\Delta H = -57.1 \times \frac{10}{1000} \text{ KJ}$$

Q → find rise in temp. when 100 ml, 0.1 M NaOH reacts with 100 ml, 0.1 M H_2SO_4 ?

\downarrow \downarrow
 0.2 N $\rightarrow 20 \text{ meq.}$

$$s(\text{water}) = 4.2 \text{ J K}^{-1} \text{ gm}^{-1}$$

$$\rho_{\text{H}_2\text{O}} = 1 \text{ g/ml}$$

$$q_p = \Delta H = m_s \Delta T = n C \Delta T$$

$$V_{\text{H}_2\text{O}} = 200 \text{ ml}$$

$$\rho_{\text{H}_2\text{O}} = \frac{m}{V_{\text{H}_2\text{O}}} \quad [m = 200 \text{ g}]$$

$$\Delta H = \left| -57.1 \times \frac{10}{1000} \times 1000 \text{ J} \right| = \text{heat absorbed by water}$$

$$|-57.1 \times 10| = m \times s \times \Delta T$$

$$\frac{57.1 \times 10}{200 \times 4.2} = \Delta T$$

(4) Enthalpy of ionization (ΔH_i)

heat or enthalpy (+ve) change to convert or dissociate 1 mole weak electrolyte (Weak Acid or Weak Base) completely into ions

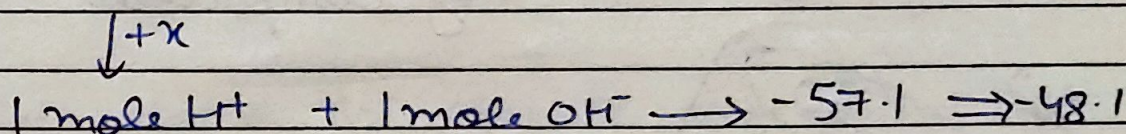
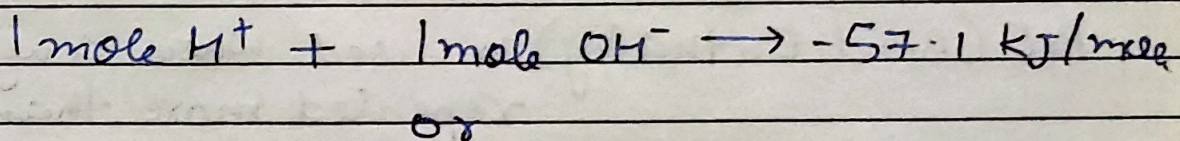
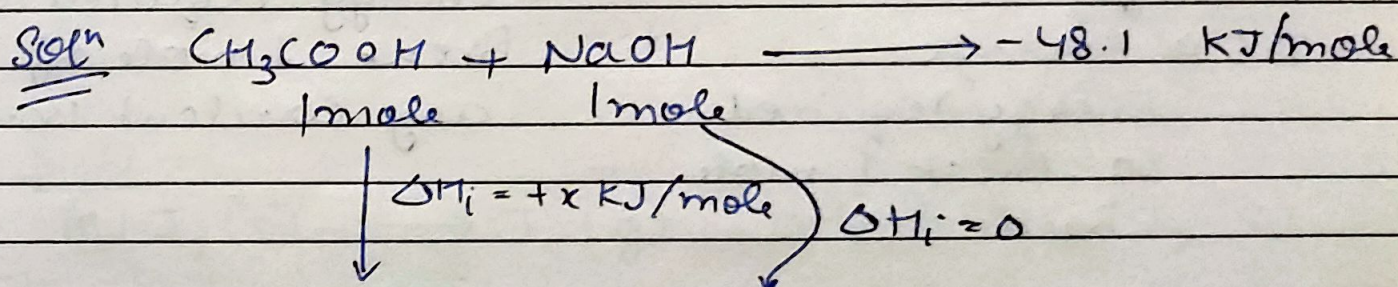
$$\Delta H_i \text{ (strong, electrolyte)} = 0$$

S.A, S.B, all salt

$$\Delta H_i \text{ (Weak Electrolyte)} \neq 0$$

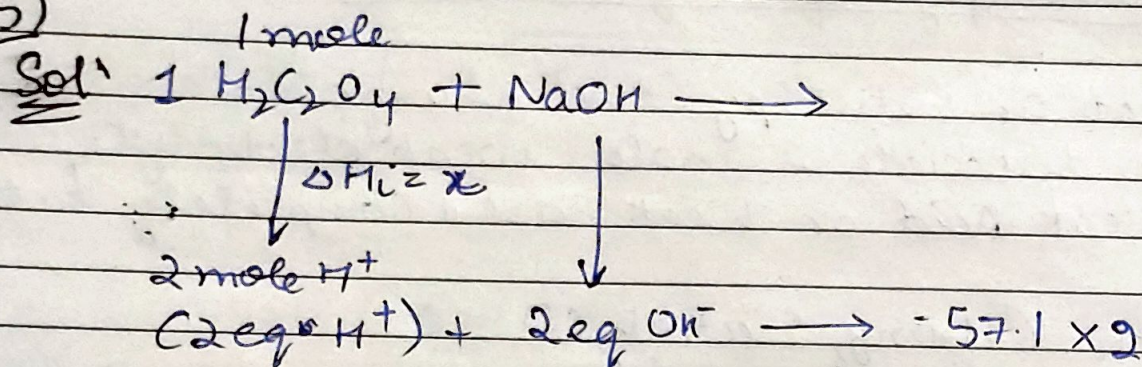
Q $\Rightarrow \Delta H_i \text{ (CH}_3\text{COOH)} = ?$

if 1 mole of CH₃COOH is mixed with 1 mole NaOH & heat of neutralization is -48.1 kJ.



$$x + (-57.1) = -48.1$$

$$\boxed{x = 9 \text{ kJ/mole}}$$



$$x - (-57.1 \times 2) = (-53.35 \times 2)$$

$$x = 8$$

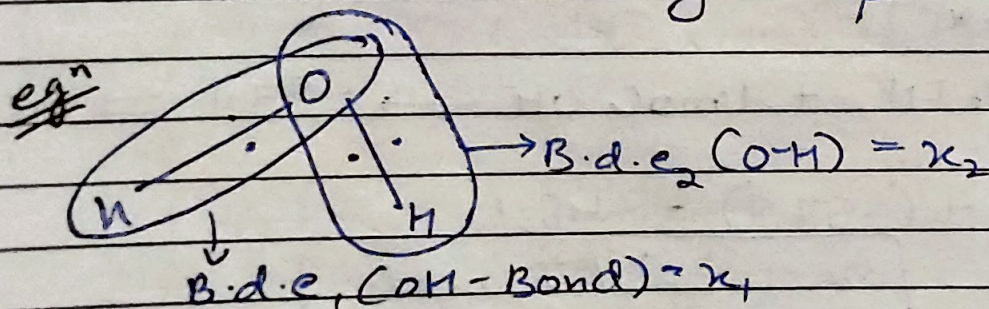
Concept of Bond dissociation enthalpy and Bond energy

B.E \Rightarrow Average
Energy required
to Break 1 mole
Bond.

B.D.E

Energy required to
Break 1 mole of
any covalent Bond.

B.E (Bond Enthalpy) is used when any Bond is repeated more than once in any compound.

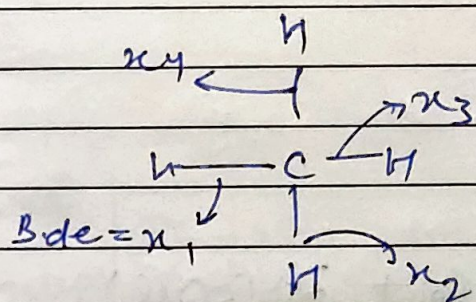
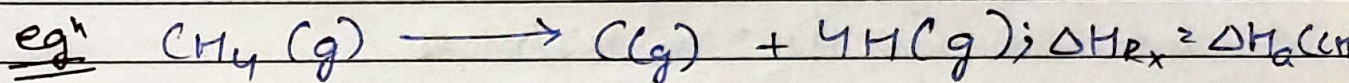


$$\text{B.E. (O-H)} = \frac{\text{B.d.e.}_1 + \text{B.d.e.}_2}{2} = \frac{x_1 + x_2}{2}$$

Note:- ΔH_a (Enthalpy of atomization)

enthalpy change when 1 mole of any substance
(+) (s, l, g)

is completely converted gaseous atoms.



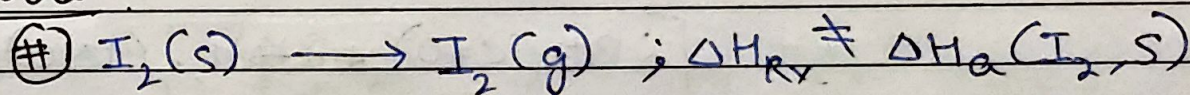
$$\approx x \text{ kJ/mole}$$

$$\approx x_1 + x_2 + x_3 + x_4$$

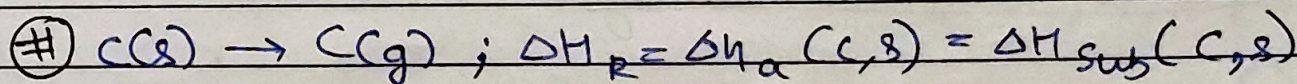
$$\text{B.E (C-H)} = \frac{x_1 + x_2 + x_3 + x_4}{4}$$

$$\approx \frac{x}{4} = \frac{\Delta H_a(\text{CH}_4)}{4}$$

Note +



$$\Delta H_{\text{Rx}} = \Delta H_{\text{sublimation}}(\text{I}_2, \text{s})$$



Note :- ΔH of any Rx^n can be represented in terms of B.E data of Reactants and Products (Provided Reactants & Products are present in Gaseous state)

$$\Delta H_{rx} = \sum \text{B.E data of Reactants} - \sum \text{B.E data of Products}$$

Q Combustion of CH_4

$$\Delta H_c(\text{CH}_4) = ?$$

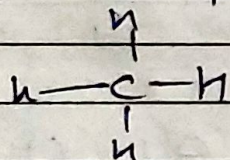
Given :- B.E (C-H) = x_1 kJ/mole

B.E (O=O) = x_2 "

B.E (C=O) = x_3 "

B.E (O-H) = x_4 "

ΔH_{vap} ~~for~~ ($\text{H}_2\text{O}, \ell$) = x_5 "



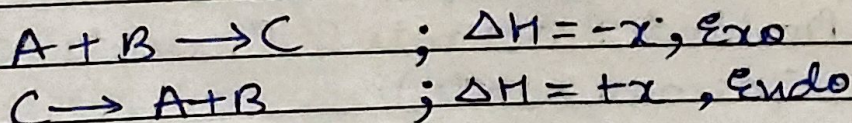
$$\Delta H_{rx} = \Delta H_c(\text{CH}_4) = ?$$

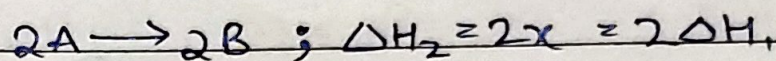
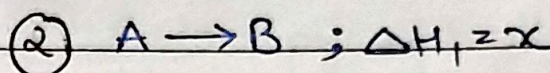
$$\Delta H_c(\text{CH}_4) = \Delta H_{rx} = 4\text{B.E}(\text{C-H}) + 2\text{B.E}(\text{O=O})$$

$$\left[2\text{B.E}(\text{C=O}) + 2\Delta H_{\text{vap}}(\text{H}_2\text{O}) + 4\text{B.E}(\text{O-H}) \right]$$

(#) Laws of Thermochemistry :-

① Lavoisier law \rightarrow Reversing the rxn Entropy change sign reverses

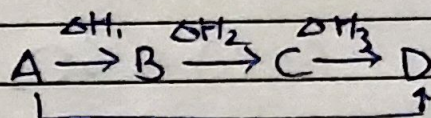
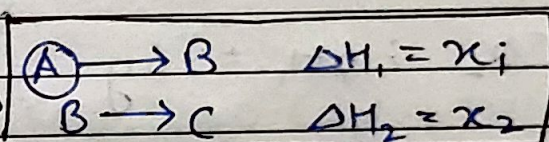




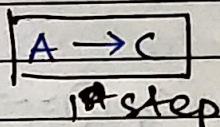
Imp.

(3) Hess's law \rightarrow The enthalpy change in a chemical or physical process is same whether the process is carried out in one step or in several steps.

egⁿ
2 steps



$$x = \Delta H_{\text{net}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$



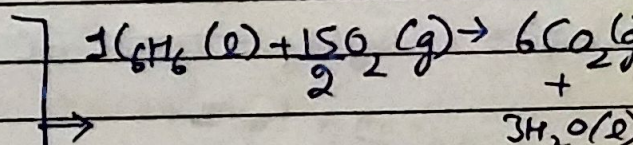
$\Delta H = \Delta H_1 + \Delta H_2 = x_1 + x_2$
--

Q $\Delta H_c (C_6H_6, l) = ?$

given $\div \Delta H_f (H_2O, l) = -x$

$\Delta H_f (CO_2, g) = -y$

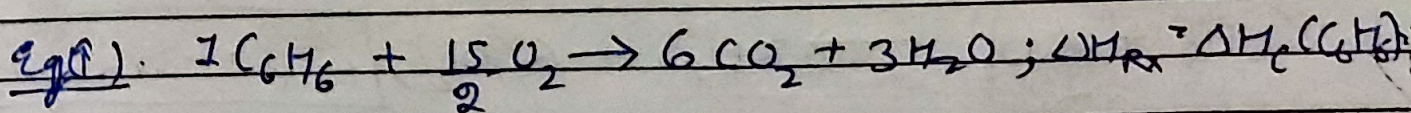
$\Delta H_f (C_6H_6, l) = -z$



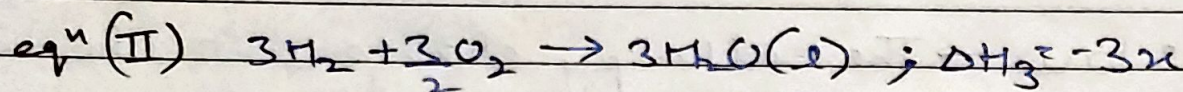
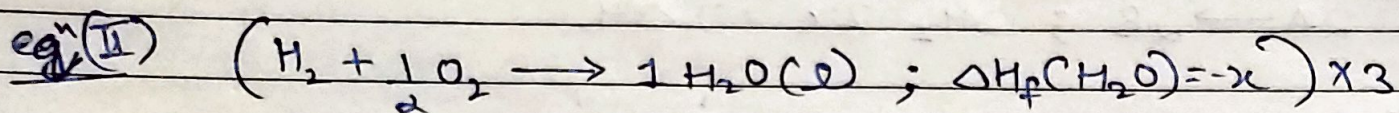
$$\Delta H_{rx} = \Delta H_c(C_6H_6)$$

$$\Delta H_c(C_6H_6) = -3x - 6y + z$$

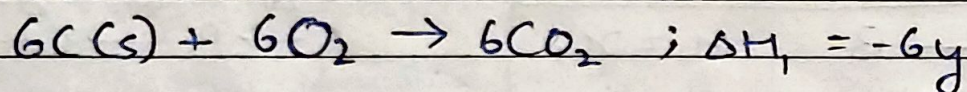
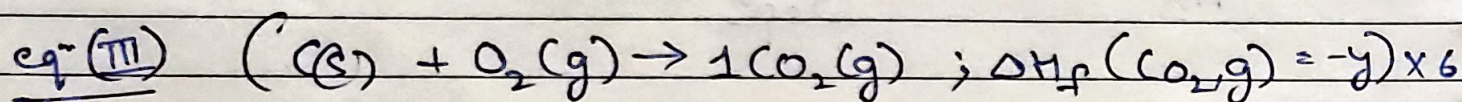
Solⁿ Combustion of Rxⁿ for C_6H_6



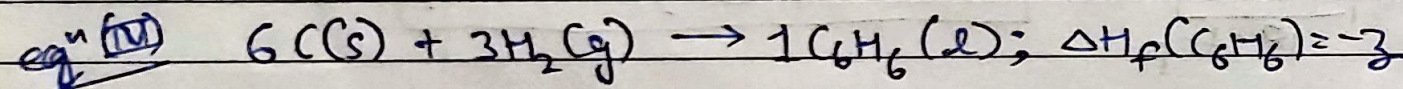
Given \div H_2O formation \div



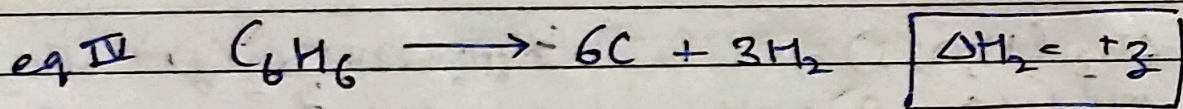
CO_2 formation



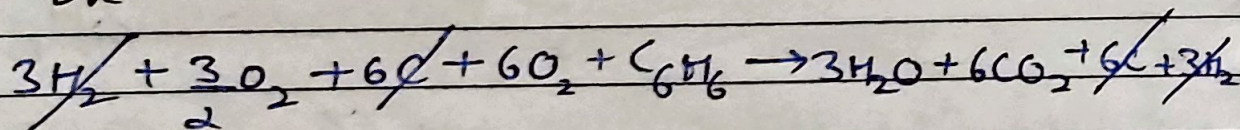
C_6H_6 formation \div



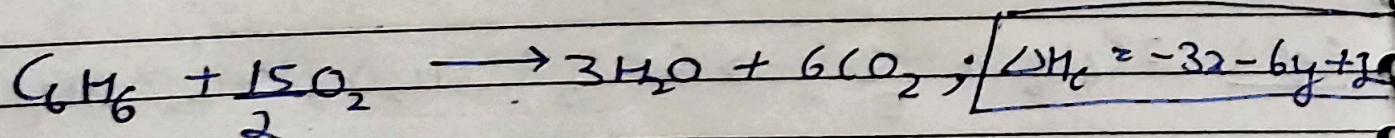
Reverse Eq IV



Add eqⁿ III + eqⁿ IV
eqⁿ (II)



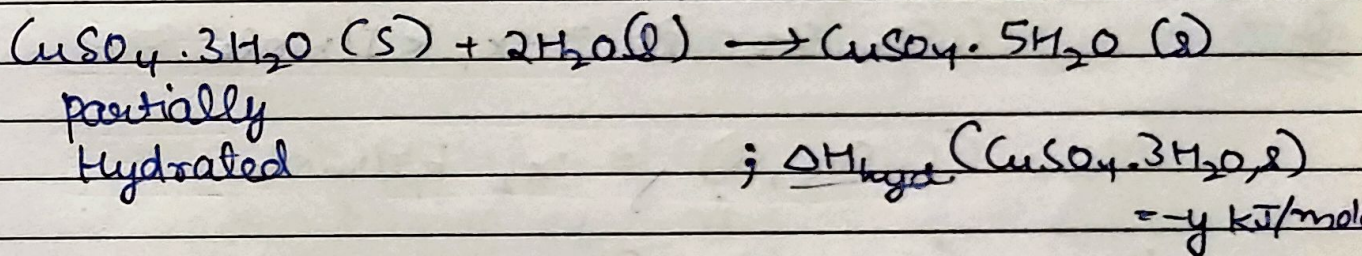
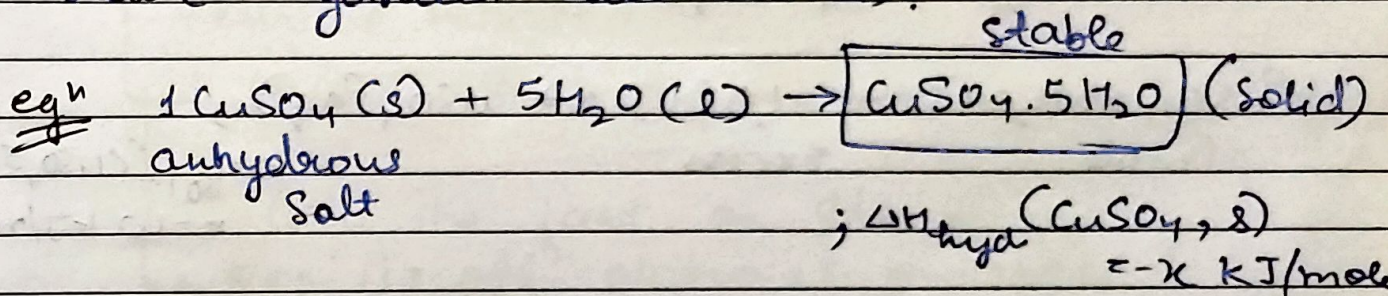
$\Delta H_c(C_6H_6) \Rightarrow \Delta H_{net} = -3x - 6y + z$



(3) Enthalpy of Hydration of Compound (ΔH_{hyd})

no water

Enthalpy change when 1 mole of a given anhydrous or partially hydrated salt is allowed to combine with required no. of moles of water molecules to form a specific stable hydrated salt (solid).

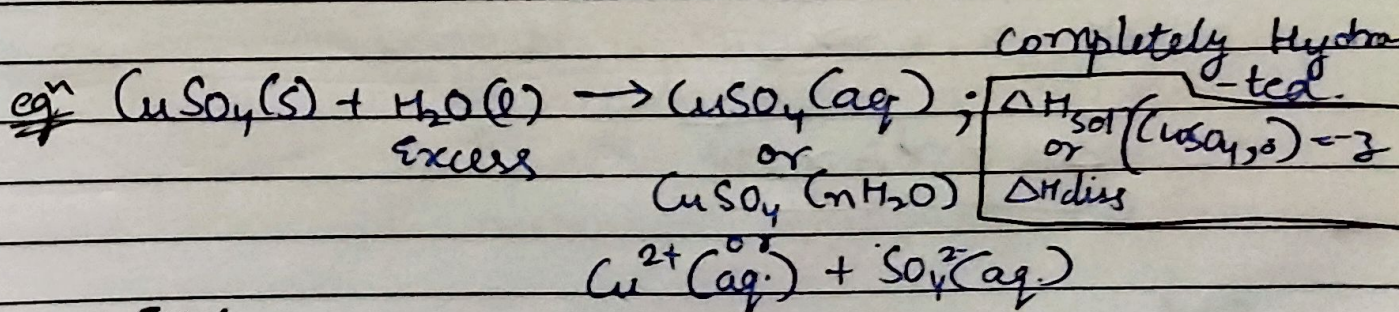


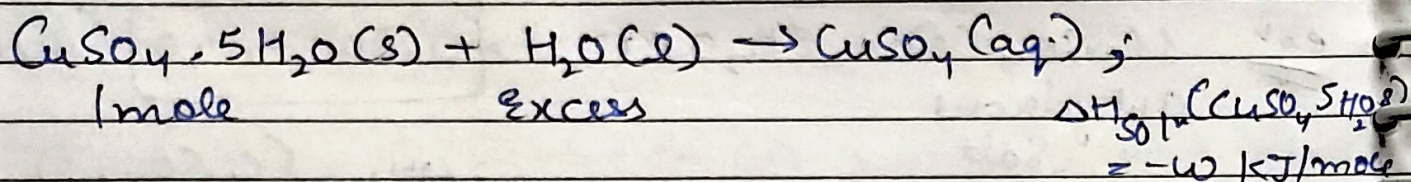
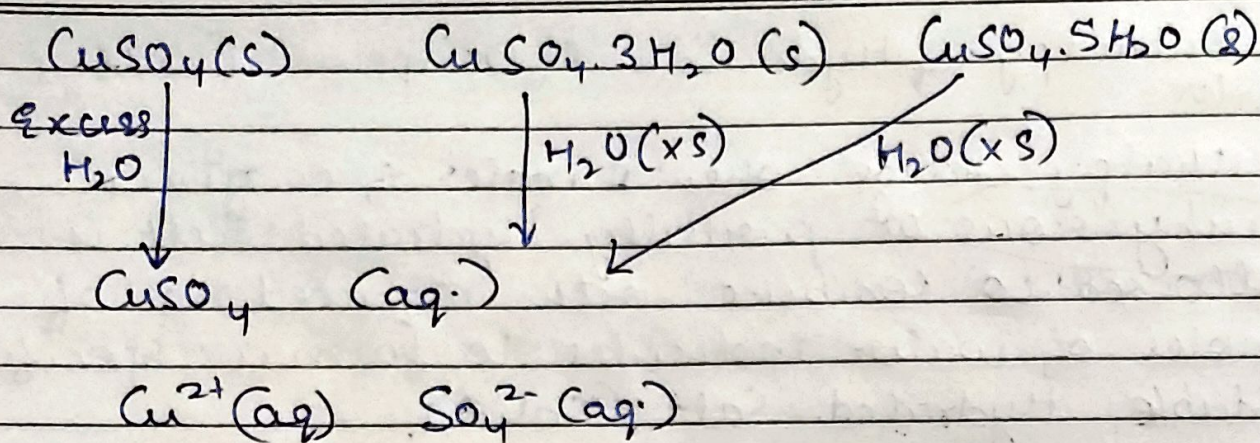
$$\boxed{|x| > |-y|}$$

When compound is solid

(4) Enthalpy of Solution or dissolution

Enthalpy change 1 mole of substance is completely dissolved in excess of solvent. → can be anhydrous, partially hydrated or completely hydrated

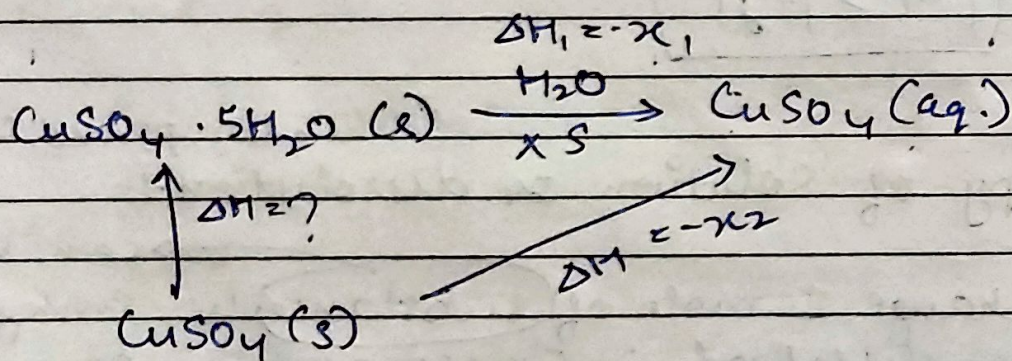




Q $\rightarrow \Delta H_{\text{soln}}(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}, \text{s}) = -x_1 \text{ kJ/mole}$

$\Delta H_{\text{soln}}(\text{CuSO}_4, \text{s}) = -x_2 \text{ kJ/mole}$

$\Delta H_{\text{hyd}}(\text{CuSO}_4, \text{s}) = ?$



$\Delta H + \Delta H_1 = \Delta H_2$

$\Delta H - x_1 = -x_2$

$\Delta H = x_1 - x_2$

★ Spontaneous Process

→ are those process which occur on its own without any constant external support.

→ can be initiated.

→ Irreversible (proceed in one direction)

→ Can be fast or slow

→ e.g. (i) all Natural processes.
(earthquake, rain, increase in Height of mountain)

(ii) Diffusion of Gas

(iii) Mixing of Gas

(iv) waterfall

(v) Burning of Gasoline, petrol, diesel etc

(**) Entropy (S) → State function

→ Extensive property

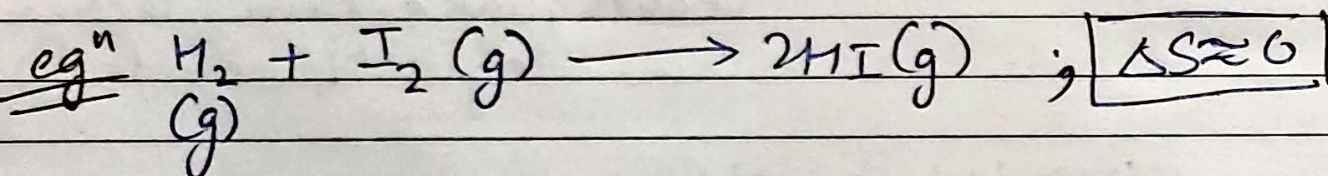
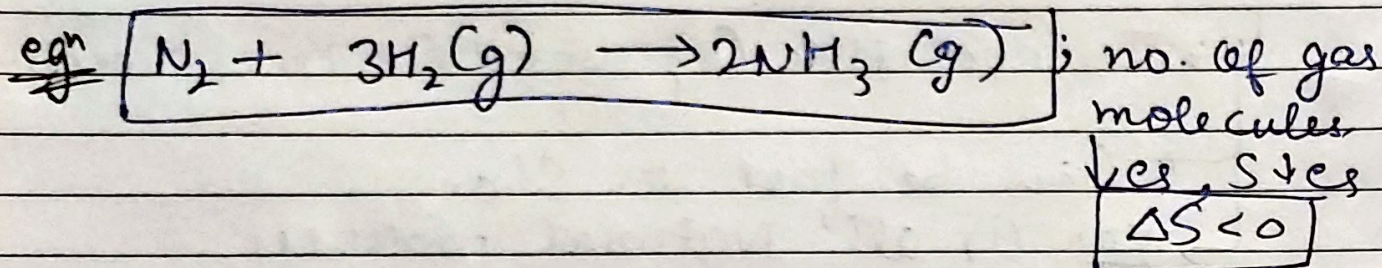
→ Defined to explain spontaneity of process.

→ It is measure of degree of randomness or disorder or patternless behaviour for maximum dissipation of Energy.

at a given Temp,

$$\Rightarrow S(\text{gas}) \gg S(\text{liq}) > S(\text{solid})$$

\Rightarrow for a Rxⁿ in System, no. of gaseous moles \uparrow es, $S \uparrow$ es, $\Delta S_{\text{system}} > 0$



\Rightarrow for isotopes, more Mass No. \rightarrow More S

\Rightarrow Crystallization process \Rightarrow $\text{liq.} \rightarrow \text{Solid}$, $S \downarrow$ es, $\Delta S < 0$

\Rightarrow Melting of ice \Rightarrow Solid \rightarrow liq ; $S \uparrow$ es, $\Delta S > 0$

★ Imp

\Rightarrow Boiling of egg $\Rightarrow S \uparrow$ es, $\Delta S > 0$

\rightarrow Due to high temp, protein molecules Breaks & no. of molecules \uparrow es, So more randomness.
 \nearrow Denaturation of Protein

⇒ Stretching of Rubber / Spring

flexibility ↓ on stretching, So $\Delta S < 0$

2nd Law of Thermodynamics ÷

Limitation of 1st Law → Energy change takes place But direction of change is not defined.

Process
or $R \times n$

will move in that direction where Entropy of Universe is continuously increasing ↓

Sys. + Surroundings

for Spontaneous process or feasible process (Irreversible)

Total Entropy change > 0 ⇒ for non-isolated system
↓
Universe

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

$$\Delta S_{\text{universe}} > 0$$

or

$$\Delta S_{\text{Total}} > 0$$

for isolated system

$$\Delta S_{\text{sys}} > 0 \text{ for spontaneity}$$

Spontaneous process proceed in a particular dirⁿ until Total Entropy become max. & $\Delta S_{\text{Universe}} = 0$
Spiral

Reversible Rxⁿ or Process at Eqⁿ

$\Delta S_{\text{universe}} = 0$ S_{max} for system
 or ΔS_{Total}
 $\Delta S_{\text{system}} = -\Delta S_{\text{surrounding}}$

Non-spontaneous or Non-feasible process

Entropy of universe must be decreasing in non-spont. direcⁿ.

constant external support is required

$$\Delta S_{\text{universe}} < 0$$

More entropy, more stability of system at given temp.

Mathematically

$$\text{Entropy change (ds)} = \frac{dq}{T}$$

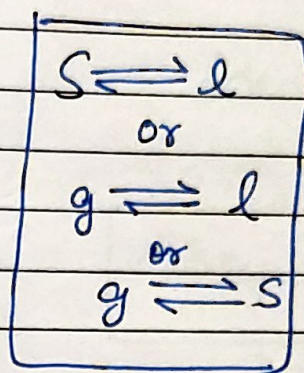
$$\Delta S = \int ds = \int \frac{dq}{T}$$

$dq \rightarrow$ Heat exchange b/w system & surrounding

$$\Delta S_{\text{system}} = \int \frac{dq_{\text{system}}}{T} \quad \Delta S_{\text{surv.}} = - \int \frac{dq_{\text{sys}}}{T}$$

Date

① Phase Change PROCESS / reaction



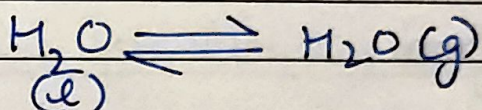
→ occur at given T. and P.

$$q_p = \Delta H$$

$$\Delta S = n \times \underbrace{\Delta H}_T$$

↑
Enthalpy of change

↓
moles of substance



$$\Delta H_{\text{vap.}} (\text{H}_2\text{O}, l) = x \text{ KJ/mol at } 100^\circ\text{C}$$

$$\Delta S = \frac{x \text{ J/K}}{373}$$

② No Phase Change

$$q = nC\Delta T \quad \text{only temp. changes}$$

$$P = \text{constant}$$

$$\Delta S = \int_T \frac{dq_p}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC dt}{T}$$

Ⓒ → Molar Heat capacity
Temp. dependent.

But if Temp. dependency not given, then consider it to be independent of temp.

(*) If C_p temp. independent

$$\Delta S = nC \ln \left[\frac{T_2}{T_1} \right]$$

(3) For ideal gas in system

changing its condition from

$$P_1, V_1, T_1 \longrightarrow P_2, V_2, T_2$$

$$\Delta S_{\text{sys.}} = \int \frac{dq}{T}$$

$$= \int \frac{dU + PdV}{T}$$

$$dq = dU + PdV$$

$$dU = dq - PdV$$

$$dU = dq + dw$$

$$\Delta S_{\text{sys.}} = nC_v \ln \left[\frac{T_2}{T_1} \right] + nR \ln \left[\frac{V_2}{V_1} \right]$$

$$\Rightarrow nC_v \ln \left[\frac{T_2}{T_1} \right] + nR \ln \left[\frac{P_1 \times T_2}{P_2 \times T_1} \right]$$

$$= nC_v \ln \left[\frac{T_2}{T_1} \right] + nR \ln \left[\frac{P_1}{P_2} \right] + nR \ln \left[\frac{T_2}{T_1} \right]$$

$$\Rightarrow n \ln \left(\frac{T_2}{T_1} \right) (C_v + R) + nR \ln \left(\frac{P_1}{P_2} \right)$$

Also, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ (Since moles of gas constant)

$$\Delta S_{\text{sys.}} = n C_p \ln \left[\frac{T_2}{T_1} \right] + nR \ln \frac{P_1}{P_2}$$

ΔS in various Process

① Isothermal Process $\Rightarrow T_1 = T_2$ $\ln \frac{T_2}{T_1} = 0$

@ Reversible
Process

Ideal gas

$$\Delta S = nR \ln \left[\frac{V_2}{V_1} \right] = -2.303 n \log \left(\frac{V_2}{V_1} \right)$$

or
 $nR \ln \left(\frac{P_1}{P_2} \right)$

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$$

$$\Delta S_{\text{sur.}} = -\Delta S_{\text{sys.}}$$

$$= \left[-nR \ln \left(\frac{V_2}{V_1} \right) \quad \text{or} \quad -nR \ln \left(\frac{P_1}{P_2} \right) \right]$$

(b) Irreversible isothermal process

$$\Delta S_{\text{total}} > 0$$

$$\text{Isothermal} \rightarrow \Delta T = 0$$

$$\Delta U = 0 = nC_V \Delta T$$

$$\Delta H = 0 = nC_P \Delta T$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

$$\Delta S_{\text{sys.}} = nR \ln \left(\frac{V_2}{V_1} \right)$$

or

$$nR \ln \left(\frac{P_1}{P_2} \right)$$

$$W_{\text{irr}} + q_{\text{irr}} = \cancel{\Delta U} \rightarrow 0$$

$$-q_{\text{irr}} = W_{\text{irr}}$$

$$\Delta S_{\text{sur.}} = \frac{(q_{\text{sys.}})_{\text{irr}}}{T}$$

$$\Delta S_{\text{sur.}} = \frac{W_{\text{irr}}}{T}$$

$$\Rightarrow \frac{-P_{\text{ext}} (V_2 - V_1)}{T}$$

$$\Rightarrow -P_{\text{ext}} \left(\frac{nRT}{T} \right) \left(\frac{1}{P_2} - \frac{1}{P_1} \right)$$

$$\Delta S_{\text{surroundings}} = -P_{\text{ext}} \times (nR) \times \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$$

(#) Adiabatic Process

$$q=0 ; \Delta S_{\text{surroundings}} = 0 \rightarrow \text{Whether rev or irr.}$$

a) Reversible

$$\Delta S_{\text{sys.}} = -\Delta S_{\text{surroundings}}$$

$$\Delta S_{\text{sys.}} = 0 = \Delta S_{\text{surroundings}}$$

b) Irreversible

$$\Delta S_{\text{sys.}} > 0$$

$$\Delta S_{\text{surroundings}} = 0$$

(?) Isochoric $V_1 = V_2$ $nR \ln \frac{V_2}{V_1} = 0$

for Ideal Gas

$$\Delta S = nC_v \ln \left(\frac{T_2}{T_1} \right)$$

(u) Isobaric $P_1 = P_2$

$$\Delta S = nC_p \ln \left(\frac{T_2}{T_1} \right)$$

**** Gibbs free Energy (G)** \rightarrow state function, Ext property

\rightarrow Energy available in the system that can be used to obtain Useful work under const. T, P .

- \rightarrow non PV work
- \rightarrow magnetic work
- \rightarrow Electrical "
- \rightarrow Rxⁿ

$$G = H - TS$$

$$(i) \Delta G_{sys} = \Delta H_{sys} - T \Delta S_{sys}$$

$$(ii) \Delta G_{sys} = -T \Delta S_{total}$$

\rightarrow Only defined for system

\rightarrow very useful Relatⁿ $\Rightarrow dG = VdP - SdT$

only T const. $dT = 0$

Isothermal

$$dG = VdP$$

$$dG = nRT \frac{dP}{P}$$

****** $\left(\frac{dG}{dt} \right)_P = -S$ ($dP = 0$)

$\left(\frac{dG}{dP} \right)_T = V$ ($dT = 0$)

$$\Delta G = nRT \ln \left(\frac{P_2}{P_1} \right)$$

$$= nR \ln \left(\frac{V_1}{V_2} \right)$$

Spon. Process \rightarrow will remain Spon. till S_{total} becomes max. & G becomes min.

$$\left[\begin{array}{l} \Delta S_{total} > 0 \\ \Delta G_{sys} < 0 \end{array} \right]$$

Rev. Process (at eqⁿ) $\Rightarrow S_{\max}, G_{\min}$

$$\boxed{\Delta S_{\text{Total}} = 0 \quad \Delta G_{\text{sys}} = 0}$$

Non Spontaneous

$$\Delta G_{\text{sys}} > 0$$

$$\Delta S_{\text{Total}} < 0$$

at

⊕ for Any Rxⁿ or Process in system

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

$$\Delta G_{\text{sys}}$$

$$\Delta H_{\text{sys}}$$

$$\Delta S_{\text{sys}}$$

i) Always -ve
(spontaneous)
(at any temp.)

-ve (exo)

+ve

(ii) Always +ve
(non spont.)
always

+ve

-ve

(iii) $|\Delta H| > |T \Delta S|$
at low Temp.
 $\Delta G = -ve$, Spont.

-ve

-ve

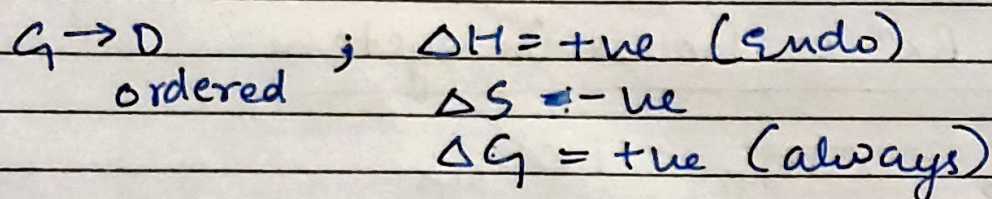
$|\Delta H| < |T \Delta S|$
at High Temp.

$\Delta G = +ve$, Non-spont.
Spiral

Date

(iv) <u>Spont.</u> at High Temp. $\rightarrow \Delta G = -ve$	$\Delta H_{sys.}$ +ve	$\Delta S_{sys.}$ +ve
<u>non-sp.</u> at low Temp. $\rightarrow \Delta G = +ve$		

** Graphite \rightarrow Diamond



$\Delta H = -ve$
 $\Delta S = -ve$

 $\rightarrow \Delta G = \Delta H - T(\Delta S)$

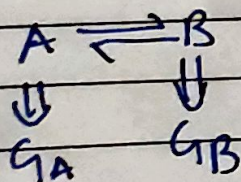
\downarrow \downarrow
 $-ve$ $+ve$

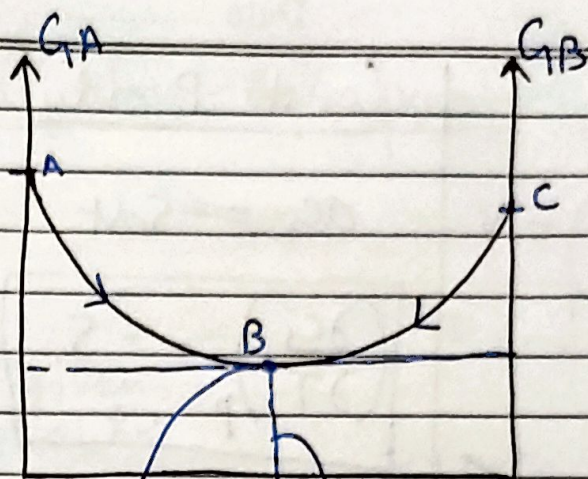
(#) Temp. at which Rx^n or Process Achieves Eq^n
 $\Delta G = 0 = \Delta H - T\Delta S$

usually Phase change

$T = \frac{\Delta H}{\Delta S}$

(#) Rev. Rx^n \rightarrow always achieves Eq^n



 G_{min} Eqⁿ point $\Delta G = 0$ Progress of
Rxn w.r.t
time

Sp. (Irr.)

$$\Delta S_{univ.} > 0$$

$$\Delta G_{sys} < 0$$

Rev \Rightarrow Eqⁿ(S_{max})_{univ.}
 G_{min}

$$\Delta S_{sys.} = \frac{\Delta H}{T}$$

$$\Delta H_{sys.} - T \Delta S_{sys.} = \Delta G = 0$$

$$\Delta S_{Total} = 0$$

$$\textcircled{\#} \quad G = H - TS$$

at const. T, P

$$\Delta G_{sys.} = \Delta H_{sys.} - T \Delta S_{sys.}$$

$$\textcircled{\#} \quad dG = VdP - SdT$$

$$G = f(T, P)$$

only T. const.

$$\boxed{dG = Vdp}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Const. P only

$$dG = -SdT$$

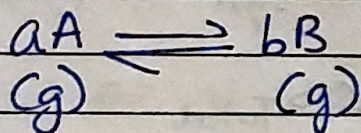
$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S}$$

for Ideal Gas

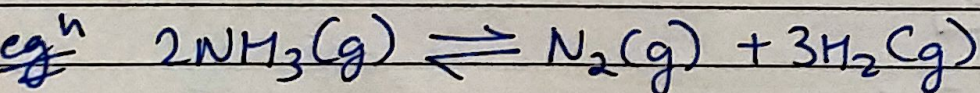
$$dG = nRT \cdot \frac{dp}{p}$$

$$\Delta G = \int dG = nRT \int \frac{dp}{p}$$

$$\boxed{\Delta G = nRT \ln \frac{P_2}{P_1}}$$

⊕ Rev. $R \times^n$ 

$$K_{eq} = K_c^n \text{ const.} = \frac{[B]^b}{[A]^a}$$



$$K_{eq} = \frac{[N_2]^1 [H_2]^3}{[NH_3]^2}$$

$[N_2]$ = molarity of N_2

$$= \frac{n_{N_2}}{V}$$

Vol. of container

At Non- Eq^n point \Rightarrow Free Energy is still available
 $\Delta G \neq 0$

$\Rightarrow \text{Conc Ratio} \neq K_{eq}$

at given cond. of Rxn
 T, P \nearrow
 $\Delta G = \Delta G^\circ$ \nwarrow at std. state

$\Rightarrow \text{Conc Ratio} = \text{Reaction Quotient } (Q)$

At $\text{Eq}^n \Rightarrow \Delta G = 0$, $Q = K_{eq}$

$\Delta G^\circ \rightarrow$ may or may not be zero

$$Q = K_{eq}$$

$$0 = \Delta G^\circ + RT \ln(K_{eq})$$

$$\frac{-\Delta G^\circ}{RT} \rightarrow \ln(K_{eq})$$

$$\frac{-\Delta G^\circ}{RT} = 2.303 \log(K_{eq})$$

$$(K_{eq} = e^{\frac{-\Delta G^\circ}{RT}})$$

$$K_{eq} = 10^{\left(\frac{-\Delta G^\circ}{2.303 RT}\right)}$$

or
or

$$K_{eq} = \text{anti log} \left(\frac{-\Delta G^\circ}{2.303 RT} \right)$$

*** Third law of Thermodynamics

At 0K (Absolute zero) Entropy of perfectly crystalline substance is zero.

$$S_{0 \text{ Kelvin}} = 0$$

Exception :-

Cl₂ (Solid)
CO (Solid)
NO (Solid)
H₂O (Solid)
H₂ (Solid)

$$\rightarrow S_{0K} \neq 0$$

there must be some residual entropy due to random arrangement

due to existence of ortho & para form

CO CO CO
CO OC CO
CO CO OC

Randomness

Due to 3rd law, Absolute value of entropy can be obtained provided molar Heat Capacity is temp. dependent.

Solid Sub (A) \longrightarrow Solid Subst. (A)
0K T K

$$\Delta S = \int_{S(0K)}^{S(TK)} dS = n \int_{T_1=0K}^{T_2=TK} \frac{C dT}{T}$$

C can be like $aT^2 + bT$

$$S_{TK} - S_{OK} = n \int_{T_1}^{T_2} \frac{c dT}{T}$$

⊕ Zeroth law of Thermo

If Body A & B are in thermal Eqⁿ, B & C are in thermal Eqⁿ, then A & C must be in thermal Eqⁿ.

$$T_A = T_B$$

$$T_B = T_C$$

then $T_A = T_C$